Chapter 3
PCBs/trans-Nonachlor in Atmospheric Components

3.1 Results

Atmospheric samples were collected from November 1993 to October 1995 at nine sampling stations on the shoreline of Lake Michigan, three stations outside of the Lake Michigan basin, 17 stations in the open lake (over-water), and two stations in Green Bay, and analyzed for PCB congeners (Table 3-1) and *trans*-nonachlor (Table 3-2). Results for "total PCBs" were determined by summing the results for the individual PCB congeners. These analytes were measured in four separate atmospheric media or phases: vapor (pg/m^3), particulates (pg/m^3), precipitation (pg/L), and dry deposition (pg/m^2). In total, 306 vapor-phase samples, 235 particulate samples, 209 precipitation samples, and 42 dry deposition samples were collected and analyzed for PCBs. For *trans*-nonachlor, 303 vapor-phase samples, 220 particulate samples, 206 precipitation samples, and 40 dry deposition samples were collected and analyzed. Eighteen of the particulate samples analyzed for PCBs and *trans*-nonachlor were collected while the *R/V Lake Guardian* was steaming between stations. Because these samples were not collected at fixed locations, they are considered spatial composites and are listed as such in Tables 3-1 and 3-2.

As noted in Chapter 2, there are 209 possible PCB congeners, and the investigators in this study reported results for 65 to 110 of these congeners, depending on the capabilities of each laboratory. For the purposes of this report, we are presenting summaries of the results for the following subset of analytes:

- PCB congener 33
- PCB congener 118
- PCB congener 180
- Total PCBs
- *trans*-nonachlor

Table 3-1. Number of Atmospheric Samples Collected and Analyzed for PCB Congeners and Total PCBs

Sampling Station		Sampling Dates	Vapor Samples Analyzed	Particulate Samples Analyzed	Dry Deposition Samples Analyzed	Precipitation Samples Analyzed	Total Samples Analyzed
Shoreline Atmospheric Stations	Beaver Island	03/15/94 to 09/26/95	19	18	0	20	57
	Chicago SWFP Crib Intake	07/01/94 to 10/03/95	0	0	9	0	9
	Chiwaukee Prairie	03/15/94 to 10/02/95	21	21	0	20	62
	IIT Chicago	12/06/93 to 10/02/95	25	25	13	17	80
	Indiana Dunes	03/15/94 to 10/20/95	31	30	0	21	82
	Manitowoc	03/12/94 to 10/08/95	19	19	0	20	58
	Muskegon	03/15/94 to 10/13/95	18	16	0	20	54
	Sleeping Bear Dunes	11/23/93 to 10/07/95	35	15	8	16	74
	South Haven	11/23/93 to 10/08/95	22	19	11	21	73
Out-of-Basin Atmospheric Stations	Bondville	03/15/94 to 10/20/95	21	21	0	21	63
	Brule River	04/01/94 to 10/08/95	19	18	0	19	56
	Eagle Harbor	04/01/94 to 07/31/94	8	4	0	4	16
Over-Water Atmospheric Stations	Spatial composites	04/30/94 to 10/11/95	0	18	0	0	18
	Empire Michigan	04/01/94 to 07/29/94	10	4	0	4	18
	GB17	04/12/95 to 04/12/95	0	0	0	1	1
	GB24M	10/17/94 to 09/20/95	4	2	0	1	7
	Harrison Crib	08/11/94 to 08/11/94	0	0	1	0	1
	1	05/10/94 to 10/11/95	5	1	0	1	7
	5	05/11/94 to 10/10/95	6	3	0	1	10
	6	08/25/94 to 10/12/95	4	1	0	0	5
	110	04/08/95 to 09/23/95	3	0	0	0	3

Sampling Station		Sampling Dates	Vapor Samples Analyzed	Particulate Samples Analyzed	Dry Deposition Samples Analyzed	Precipitation Samples Analyzed	Total Samples Analyzed
Over-Water Atmospheric Stations	18M	05/06/94 to 10/09/95	5	0	0	0	5
	23M	05/04/94 to 10/03/95	4	0	0	1	5
	27M	05/02/94 to 09/27/95	5	0	0	0	5
	280	10/26/94 to 10/01/95	4	0	0	0	4
	310	03/28/95 to 10/08/95	3	0	0	0	3
	380	10/31/94 to 01/23/95	1	0	0	1	2
	40M	10/18/94 to 09/25/95	4	0	0	0	4
	41	04/30/94 to 08/12/94	2	0	0	0	2
	47M	08/07/94 to 09/19/95	5	0	0	0	5
	MB19M	01/24/95 to 01/24/95	1	0	0	0	1
	11M	05/08/94 to 05/08/94	2	0	0	0	2
Total			306	235	42	209	792

Table 3-2. Number of Atmospheric Samples Collected and Analyzed for *trans*-Nonachlor

Sampling Station		Sampling Dates	Vapor Samples Analyzed	Particulate Samples Analyzed	Dry Deposition Samples Analyzed	Precipitation Samples Analyzed	Total Samples Analyzed
Shoreline Atmospheric Stations	Beaver Island	03/15/94 to 09/26/95	18	17	0	20	55
	Chicago SWFP Crib Intake	07/01/94 to 10/03/95	0	0	9	0	9
	Chiwaukee Prairie	03/15/94 to 10/02/95	21	21	0	20	62
	IIT Chicago	12/06/93 to 10/02/95	25	25	13	17	80
	Indiana Dunes	03/15/94 to 10/20/95	31	29	0	21	81
	Manitowoc	03/12/94 to 10/08/95	19	18	0	20	57
	Muskegon	03/15/94 to 10/13/95	18	16	0	19	53
	Sleeping Bear Dunes	11/23/93 to 10/07/95	34	4	8	14	60
	South Haven	11/23/93 to 10/08/95	22	18	10	21	71
Out-of-Basin Atmospheric Stations	Bondville	03/15/94 to 10/20/95	21	21	0	21	63
	Brule River	04/01/94 to 10/08/95	18	18	0	19	55
	Eagle Harbor	04/01/94 to 07/31/94	8	4	0	4	16
Over-Water Atmospheric Stations	Spatial composites	04/30/94 to 10/11/95	0	18	0	0	18
	Empire Michigan	04/01/94 to 07/29/94	10	4	0	4	18
	GB17	04/12/95 to 04/12/95	0	0	0	1	1
	GB24M	10/17/94 to 09/20/95	4	2	0	1	7
	1	05/10/94 to 10/11/95	5	1	0	1	7
	5	05/11/94 to 10/10/95	6	3	0	1	10
	6	08/25/94 to 10/12/95	4	1	0	0	5
	110	04/08/95 to 09/23/95	3	0	0	0	3
	18M	05/06/94 to 10/09/95	5	0	0	0	5

Sampling Station		Sampling Dates	Vapor Samples Analyzed	Particulate Samples Analyzed	Dry Deposition Samples Analyzed	Precipitation Samples Analyzed	Total Samples Analyzed
Over-Water Atmospheric Stations	23M	05/04/94 to 10/03/95	4	0	0	1	5
	27M	05/02/94 to 09/27/95	5	0	0	0	5
	280	10/26/94 to 10/01/95	4	0	0	0	4
	310	03/28/95 to 10/08/95	3	0	0	0	3
	380	10/31/94 to 01/23/95	1	0	0	1	2
	40M	10/18/94 to 09/25/95	4	0	0	0	4
	41	04/30/94 to 08/12/94	2	0	0	0	2
	47M	08/07/94 to 09/19/95	5	0	0	0	5
	MB19M	01/24/95 to 01/24/95	1	0	0	0	1
	11M	05/08/94 to 05/08/94	2	0	0	0	2
Total			303	220	40	206	769

3.1.1 Vapor Fraction

Vapor-phase PCB congeners were detected in the vast majority of the samples collected from all LMMB Study stations. Vapor-phase PCB 33 was detected in all but two samples (Table 3-3), vapor-phase PCB 118 was detected in all but one sample (Table 3-4), and vapor-phase PCB 180 was detected in all but five samples (Table 3-5). Tables 3-3 to 3-6 present the results for the monthly composite vapor samples from this study. As discussed in Chapter 2, the composite results represent either: 1) the physical compositing of several individual samples collected during a calendar month to create one sample for analysis, or 2) mathematical composites of the results from the analysis of the individual samples collected over a calendar month. In some instances, both physical and mathematical composites were prepared within a month. In these instances, the reported result is a mathematical composite based on both the physical composite samples and the individual samples. The total number of composite results is shown for each station as "N," along with the mean concentration, range, standard deviation, and relative standard deviation (RSD). Tables 3-3 to 3-6 also indicate the percent of the *individual* sample results that were below the sample-specific detection limit, (as opposed to the percent of the composite results). The mean concentrations were calculated using the results reported by each laboratory (substitution of the detection limit or other value was not used for results below the sample-specific detection limits).

Monthly composite vapor-phase PCB congener concentrations ranged from 0 pg/m^3 for PCB 180 at the Sleeping Bear Dunes and Brule Rivers stations and open-water station 27M, to 290 pg/m^3 for PCB 33 at the IIT Chicago sampling station (Tables 3-3 to 3-5). Monthly composite concentrations of vapor-phase total PCBs ranged from 0 pg/m^3 at Beaver Island and Brule River stations to 6300 pg/m^3 at the IIT

Chicago station (Table 3-6). Mean monthly composite concentrations of vapor-phase PCBs ranged from 0.24 pg/m^3 for PCB 180 at Sleeping Bear Dunes to 2600 pg/m^3 for total PCBs at the IIT Chicago site.

The variability of the monthly composite concentrations differed among both stations and congeners, with RSD values ranging from 32% to 150% for PCB 33, from 15% to 170% for PCB 118, and 45% to 160% for PCB 180. Except for vapor-phase results for PCBs 118 and 180 at Indiana Dunes, and the PCB 33 results at Sleeping Bear Dunes, many of the highest RSD values are associated with sampling stations with small numbers of total samples, particularly for the over-water stations and the remote shore-based site at Eagle Harbor, suggesting that one of the monthly composite results may be driving the variability.

For stations with greater than 10 samples over the course of the study, the variability for vapor-phase PCB 33 was greatest at Sleeping Bear Dunes (RSD = 120%) and greatest for PCB 118 and PCB 180 at Indiana Dunes (RSDs of 140% and 150%, respectively).

Vapor-phase *trans*-nonachlor was detected much less frequently than PCB congeners (Table 3-7). Vapor-phase *trans*-nonachlor was not detected in the samples from two over-water stations. Of the 28 sampling stations, 13 stations had 13% to 50% of the individual samples below detection limits. Only one sample was collected at Stations 380 and MB19M and each had a result of zero.

Concentrations of vapor-phase *trans*-nonachlor ranged from 0 pg/m^3 at over-water stations 380 and MB19M to 118 pg/m^3 at Bondville. Non-zero mean monthly composite concentrations of *trans*-nonachlor for each sampling station ranged from 2.1 pg/m^3 measured at Brule River to 43 pg/m^3 measured at Bondville.

Table 3-3. Monthly Composite Concentrations of Vapor-phase PCB 33 Measured in Samples Collected Around Lake Michigan from April 1994 to October 1995

Sampling Station		N	Mean (pg/m^3)	Range (pg/m^3)	SD (pg/m^3)	RSD (%)	% Below DL*
Shoreline Atmospheric Stations	Beaver Island	18	20	2.1 to 54	17	83	0
	Chiwaukee Prairie	19	14	2.0 to 35	9.3	66	0
	IIT Chicago	19	130	24 to 290	87	69	0
	Indiana Dunes	19	39	4.6 to 120	30	76	0
	Manitowoc	19	16	2.4 to 48	13	80	0
	Muskegon	18	21	2.6 to 71	17	83	0
	Sleeping Bear Dunes	11	10	2.0 to 44	12	120	0
	South Haven	19	17	3.4 to 37	11	64	0
Out-of-Basin Atmospheric Stations	Bondville	19	41	4.0 to 130	33	80	10
	Brule River	18	6.1	0.62 to 21	5.7	94	0
	Eagle Harbor	4	4.9	0.89 to 12	5.0	100	0
Over-Water Atmospheric Stations	Empire Michigan	4	6.4	4.3 to 8.7	2.2	34	0
	GB24M	3	27	3.5 to 72	39	150	0
	1	3	31	8.0 to 51	22	70	0
	5	4	37	20 to 55	14	38	0
	6	3	25	16 to 30	7.8	32	0
	110	3	20	2.1 to 54	29	140	0
	18M	3	43	7.8 to 100	53	120	0
	23M	2	31	23 to 40	12	37	0
	27M	3	19	6.0 to 34	14	76	0
	280	3	20	7.0 to 45	22	110	0
	310	3	26	10 to 53	23	91	0
	380	1	10	NA	NA	NA	0
	40M	3	13	2.0 to 28	13	100	0
	47M	3	22	4.6 to 51	25	110	0
	MB19M	1	10	NA	NA	NA	0
	11M	1	33	NA	NA	NA	0

* Value represents the percent of the individual samples collected and analyzed, not of the monthly composite samples prepared from the individual samples.
NA = Not applicable

Table 3-4. Monthly Composite Concentrations of Vapor-Phase PCB 118 Measured in Samples Collected Around Lake Michigan from April 1994 to October 1995

Sampling Station		N	Mean (pg/m^3)	Range (pg/m^3)	SD (pg/m^3)	RSD (%)	% Below DL*
Shoreline Atmospheric Stations	Beaver Island	18	19	1.2 to 70	21	110	0
	Chiwaukee Prairie	19	2.2	0.24 to 5.8	1.5	71	0
	IIT Chicago	19	29	3.5 to 66	22	77	0
	Indiana Dunes	19	6.8	0.58 to 33	9.2	140	0
	Manitowoc	19	2.2	0.25 to 5.0	1.5	67	0
	Muskegon	18	6.6	1.1 to 21	6.5	99	0
	Sleeping Bear Dunes	11	1.2	0.29 to 2.7	0.75	62	3.8
	South Haven	19	1.8	0.35 to 5.2	1.3	73	0
Out-of-Basin Atmospheric Stations	Bondville	19	1.6	0.43 to 2.9	0.78	50	0
	Brule River	18	0.83	0.075 to 2.8	0.85	100	0
	Eagle Harbor	4	2.9	0.20 to 9.9	4.7	170	0
Over-Water Atmospheric Stations	Empire Michigan	4	1.2	0.59 to 1.7	0.50	43	0
	GB24M	3	5.2	1.1 to 13	6.4	120	0
	1	3	39	1.3 to 110	61	160	0
	5	4	6.5	5.4 to 7.9	1.0	16	0
	6	3	42	2.2 to 120	67	160	0
	110	3	5.7	0.78 to 15	8.4	150	0
	18M	3	6.2	2.0 to 14	7.1	120	0
	23M	2	6.5	5.7 to 7.4	1.2	18	0
	27M	3	4.1	0.64 to 6.4	3.1	74	0
	280	3	4.2	1.5 to 7.1	2.8	67	0
	310	3	3.9	2.3 to 6.1	2.0	51	0
	380	1	1.0	NA	NA	NA	0
	40M	3	2.4	0.48 to 4.9	2.2	95	0
	47M	3	3.2	1.2 to 6.3	2.8	87	0
	MB19M	1	1.0	NA	NA	NA	0

* Value represents the percent of the individual samples collected and analyzed, not of the monthly composite samples prepared from the individual samples.
NA = Not applicable

Table 3-5. Monthly Composite Concentrations of Vapor-Phase PCB 180 Measured in Samples Collected Around Lake Michigan from April 1994 to October 1995

Sampling Station		N	Mean (pg/m^3)	Range (pg/m^3)	SD (pg/m^3)	RSD (%)	% Below DL*
Shoreline Atmospheric Stations	Beaver Island	18	11	0.53 to 27	9.8	92	0
	Chiwaukee Prairie	19	0.54	0.076 to 1.2	0.32	59	0
	IIT Chicago	19	4.3	0.44 to 9.2	3.3	75	0
	Indiana Dunes	19	1.6	0.13 to 8.3	2.3	150	0
	Manitowoc	19	0.47	0.059 to 1.1	0.32	68	0
	Muskegon	18	1.0	0.13 to 2.7	0.93	90	0
	Sleeping Bear Dunes	11	0.24	0.00 to 0.57	0.20	84	35
	South Haven	19	0.47	0.059 to 1.3	0.38	87	0
Out-of-Basin Atmospheric Stations	Bondville	19	0.52	0.13 to 1.1	0.30	57	0
	Brule River	18	0.27	0.00 to 0.80	0.23	87	11
	Eagle Harbor	4	0.33	0.065 to 0.81	0.33	100	13
Over-Water Atmospheric Stations	Empire Michigan	4	0.36	0.015 to 0.50	0.16	45	0
	GB24M	3	0.73	0.24 to 1.6	0.79	110	0
	1	3	16	0.90 to 45	25	160	0
	5	4	2.4	1.6 to 4.3	1.3	52	0
	6	3	15	1.1 to 43	24	160	0
	110	3	0.93	0.16 to 2.4	1.3	140	0
	18M	3	1.8	0.57 to 4.0	1.9	100	0
	23M	2	1.6	0.69 to 2.5	1.3	80	0
	27M	3	1.0	0.00 to 2.0	0.99	96	33
	280	3	1.4	0.43 to 3.1	1.5	110	0
	310	3	1.1	0.36 to 1.6	0.64	60	0
	380	1	0.47	NA	NA	NA	0
	40M	3	0.67	0.087 to 1.4	0.69	100	0
	47M	3	0.75	0.17 to 1.6	0.77	100	0
	MB19M	1	0.46	NA	NA	NA	0
	11M	1	55	NA	NA	NA	0

* Value represents the percent of the individual samples collected and analyzed, not of the monthly composite samples prepared from the individual samples.
NA = Not applicable

Table 3-6. Monthly Composite Concentrations of Vapor-Phase Total PCBs Measured in Samples Collected Around Lake Michigan from April 1994 to October 1995

Sampling Station		N	Mean (pg/m^3)	Range (pg/m^3)	SD (pg/m^3)	RSD (%)
Shoreline Atmospheric Stations	Beaver Island	19	970	0 to 2400	880	90
	Chiwaukee Prairie	19	320	47 to 810	230	72
	IIT Chicago	19	2600	460 to 6300	1900	72
	Indiana Dunes	19	680	88 to 2000	580	85
	Manitowoc	19	350	49 to 830	260	74
	Muskegon	18	490	68 to 1300	410	84
	Sleeping Bear Dunes	15	380	54 to 2000	550	150
	South Haven	19	400	54 to 1400	360	89
Out-of-Basin Atmospheric Stations	Bondville	19	250	44 to 590	150	60
	Brule River	19	110	0.00 to 390	110	99
	Eagle Harbor	4	260	29 to 800	370	140
Over-Water Atmospheric Stations	Empire Michigan	4	170	87 to 260	77	46
	GB24M	4	940	7.8 to 3400	1600	180
	1	5	990	6.0 to 3600	1500	150
	5	6	670	9.8 to 1500	590	88
	6	4	1200	52 to 3900	1800	140
	110	3	810	84 to 2200	1200	150
	18M	5	560	7.6 to 2200	930	170
	23M	4	490	21 to 1300	600	120
	27M	5	360	9.6 to 1000	410	120
	280	4	480	4.9 to 1300	570	120
	310	3	650	380 to 1200	430	67
	380	1	290	NA	NA	NA
	40M	4	340	7.6 to 1000	460	140
	41	2	21	16 to 25	6.4	31
	47M	5	410	8.5 to 1500	630	150
	MB19M	1	280	NA	NA	NA
	11M	2	2200	8.9 to 4300	3100	140

NA = Not applicable

Table 3-7. Monthly Composite Concentrations of Vapor-Phase *trans*-Nonachlor Measured in Samples Collected Around Lake Michigan from April 1994 to October 1995

Sampling Station		N	Mean (pg/m^3)	Range (pg/m^3)	SD (pg/m^3)	RSD (%)	% Below DL*
Shoreline Atmospheric Stations	Beaver Island	18	3.9	0.10 to 20	4.9	130	6
	Chiwaukee Prairie	19	9.3	0.30 to 25	8.1	86	0
	IIT Chicago	19	29	1.5 to 80	22	77	0
	Indiana Dunes	19	19	1.0 to 61	16	84	0
	Manitowoc	19	7.5	0 to 19	6.0	81	21
	Muskegon	18	14	0.40 to 51	16	110	0
	Sleeping Bear Dunes	15	5.3	0.98 to 15	4.8	86	26
	South Haven	19	10	0 to 33	8.8	86	4.5
Out-of-Basin Atmospheric Stations	Bondville	19	43	1.9 to 120	37	87	0
	Brule River	18	2.1	0 to 12	2.9	140	28
	Eagle Harbor	4	3.7	1.0 to 6.2	2.1	58	13
Over-Water Atmospheric Stations	Empire Michigan	4	8.8	5.5 to 21	3.6	41	0
	GB24M	4	2.9	0.00 to 5.1	2.3	79	25
	1	5	13	1.1 to 39	15	110	0
	5	6	14	1.8 to 28	11	81	0
	6	4	12	1.1 to 34	15	130	0
	110	3	5.2	0.0 to 14	8.0	150	33
	18M	5	8.3	0 to 31	13	150	20
	23M	4	14	3.8 to 25	10	74	0
	27M	5	5.6	0 to 14	5.2	93	20
	280	4	5.8	0 to 19	8.6	150	25
	310	3	6.8	1.9 to 16	7.6	110	0
	380	1	0	NA	NA	NA	100
	40M	4	6.6	0.20 to 14	6.2	94	0
	41	2	3.2	0 to 6.5	4.6	140	50
	47M	5	7.2	0 to 14	5.8	80	20
	MB19M	1	0	NA	NA	NA	100
	Station 11M	2	4.3	3.8 to 4.7	0.69	16	0

* Value represents the percent of the individual samples collected and analyzed, not of the monthly composite samples prepared from the individual samples.
NA = Not applicable

3.1.1.1 Temporal Variation

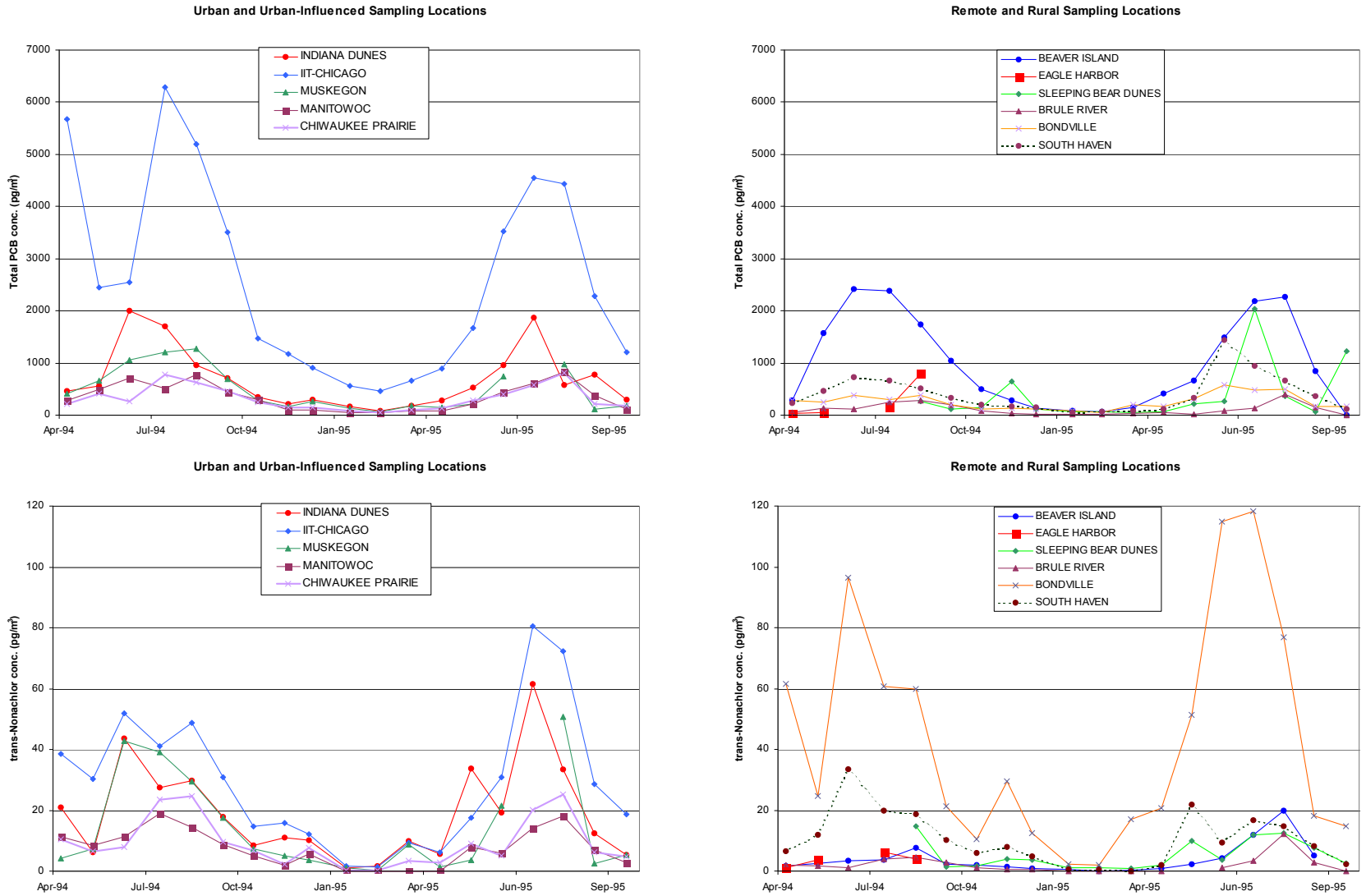
Vapor-phase PCB results exhibited a seasonal trend, with higher concentrations occurring in summer months and lower concentrations occurring in winter months (Figure 3-1). This seasonal variation has often been reported for semivolatile compounds (Hoff *et al.*, 1992, Burgoyne and Hites, 1993, and Cortes *et al.*, 1998) and may be a result of the interaction of the vapor pressures of the PCBs and the increased temperatures during summer months. The results for each monthly composite sample were plotted using the mid-point of the compositing period as the date (e.g., the date midway between the start of the collection of the first individual sample in the composite and the end of the collection of the last individual sample in the composite).

All of the sites exhibited similar trends in vapor phase total PCB concentrations, with higher concentrations generally occurring in the summer and lower concentrations in the winter, despite differences between sites of an order of magnitude or more. For example, concentrations of vapor-phase total PCBs measured at the urban-influenced site, Manitowoc, were 49 pg/m^3 in February 1995 and were 17 times higher in August 1995 at 830 pg/m^3. For the remote site, Beaver Island, vapor-phase total PCB concentrations were 72 pg/m^3 in February 1995 and were 31 times higher in August 1995, at 2300 pg/m^3.

Vapor-phase *trans*-nonachlor results showed an even stronger seasonal variation than the vapor-phase PCB results. All of the sites exhibited similar trends in vapor phase *trans*-nonachlor concentrations, with higher concentrations generally occurring in the summer and lower concentrations in the winter, despite differences between sites of an order of magnitude or more. For the urban site IIT Chicago, concentrations of vapor-phase *trans*-nonachlor were 1.5 pg/m^3 in February 1995 and were 50 times higher in July 1995, at 80 pg/m^3. For the rural Bondville station, vapor-phase *trans*-nonachlor was 2 pg/m^3 in February 1995 and was 60 times higher in July 1995 at 120 pg/m^3.

Temporal variability could not be evaluated for the over-water stations because of the limited number of composite samples (1 to 4 at any given over-water station) that do not represent either all four seasons in any one year, or the entire time-span of the LMMB Study.

Figure 3-1. Temporal Variations of Total Vapor-Phase PCB (top) and *trans*-Nonachlor (bottom) Concentrations Measured at Lake Michigan Shoreline and Out-of-Basin Stations from April 1994 to October 1995

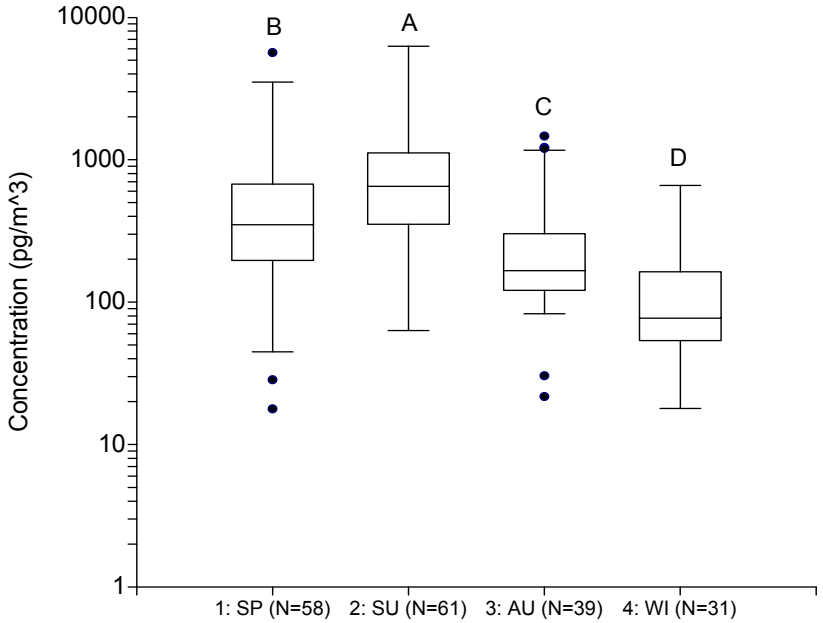


PCB congener and total PCB concentrations were significantly different among the four seasons. Seasons were defined as:

Spring (SP)	=	March 20 to June 20,
Summer (SU)	=	June 21 to September 22,
Autumn (AU)	=	September 23 to December 21, and
Winter (WI)	=	December 22 to March 19

As illustrated in Figure 3-2, the concentrations of total PCBs measured at shoreline and out-of-basin stations differed significantly between seasons ($p<0.0001$, two-way ANOVA with a Tukey pairwise comparison, total PCB concentrations were log-transformed prior to conducting the test). Concentrations of vapor-phase total PCBs are significantly higher in the summer and the seasons can be ranked in order of decreasing monthly composite vapor-phase total PCB concentration as: Summer > Spring > Autumn >Winter. Concentrations of PCB 118 and 180 also were significantly different for all seasons in the same pattern as the total PCBs.

Figure 3-2. Seasonal Differences in Vapor-phase Total PCB Concentrations Measured at Lake Michigan Shoreline and Out-of-basin Stations from April 1994 and October 1995

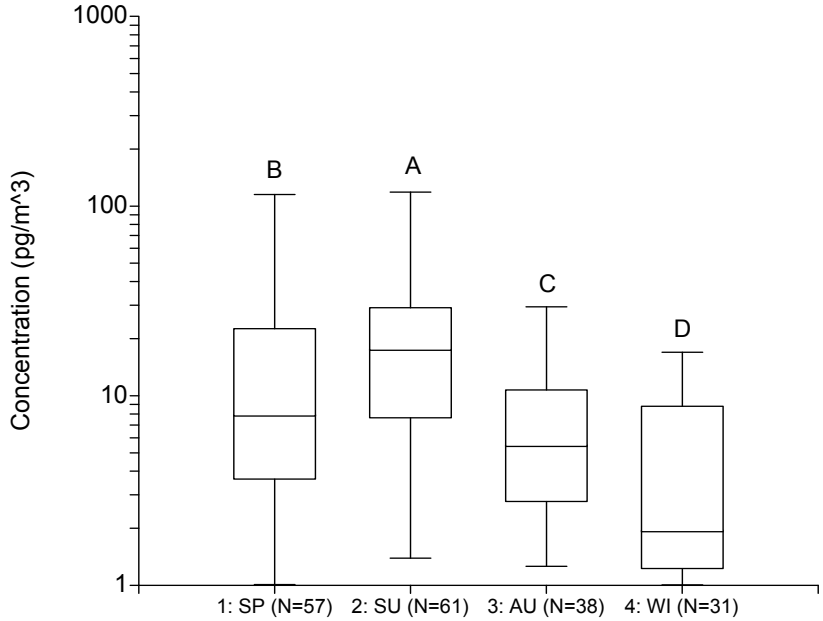


Boxes represent the 25th percentile (bottom of box), 50th percentile (center line), and 75th percentile (top of box) results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. The letters (A - D) above the boxes represent the results of the analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05). Concentration is plotted on a log scale.

For PCB 33, there was a statistically significant interaction between season and station, indicating that the variations among seasons differed for the stations. The out-of-basin stations at Bondville and Eagle Harbor and the shoreline stations at Muskegon and Sleeping Bear Dunes did not have a significant difference for vapor-phase PCB 33 among seasons. The results for all other stations exhibited some significant difference among seasons, with the same general trend as total PCBs, PCB 118 and PCB 180, in which the mean concentrations were highest in summer and lowest in winter. At Eagle Harbor, the lack of a seasonal difference likely was due to the lack of composite samples collected in autumn and winter at this remote site.

For *trans*-nonachlor, concentrations differed significantly among seasons ($p<0.0001$, two-way ANOVA with a Tukey pairwise comparison, *trans*-nonachlor concentrations were log-transformed prior to conducting the test). Mean concentrations of vapor-phase *trans*-nonachlor are significantly higher in the summer and the seasons can be ranked in order of decreasing monthly composite vapor-phase total PCB concentration as: Summer > Spring > Autumn >Winter.

Figure 3-3. Seasonal Differences in *trans*-Nonachlor Concentrations Measured at Lake Michigan Shoreline and Out-of-Basin Stations from April 1994 to October 1995



Boxes represent the 25th percentile (bottom of box), 50th percentile (center line), and 75th percentile (top of box) results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Letters above the boxes represent the results of the analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05). Concentration is plotted on a log scale.

3.1.1.2 Geographical Variation

Vapor-phase PCB congener and total PCB concentrations varied by sampling station (Table 3-9). Urban and urban-influenced sites had higher mean monthly composite concentrations for the duration of the study period than rural sites. For example, the mean vapor-phase total PCB concentrations were 2600, 460, and 400 pg/m^3, respectively, for the urban, urban-influenced, and rural stations. A similar pattern was observed for PCB 118 (Table 3-8). These data are consistent with what is expected, given that urban and urban-influenced areas contain significant sources of vapor-phase PCBs. However, the mean concentrations for total PCBs and PCB 118 at the remote sites are higher than those at the urban and urban-influenced sites. The higher mean concentration for the remote sites is largely due to the high concentration of PCBs at the Beaver Island station (Figure 3-4). The results for PCBs at Beaver Island suggest the presence of an unknown source for PCBs at this station.

The mean concentration of vapor-phase total PCBs at over-water stations was 640 pg/m^3 (Table 3-8), which is higher than the mean concentrations for the urban-influenced, out-of-basin, and rural stations (460, 190, and 400 pg/m^3, respectively). The mean concentration of vapor-phase PCB 118 at over-water stations was also higher than the other station types (Table 3-8). However, the mean concentrations of

PCB at the over-water stations may be driven by the relatively high concentrations observed at Stations 1,5,6, and 11M (Tables 3-3 to 3-6), which are all fairly close to shore in the area near Chicago.

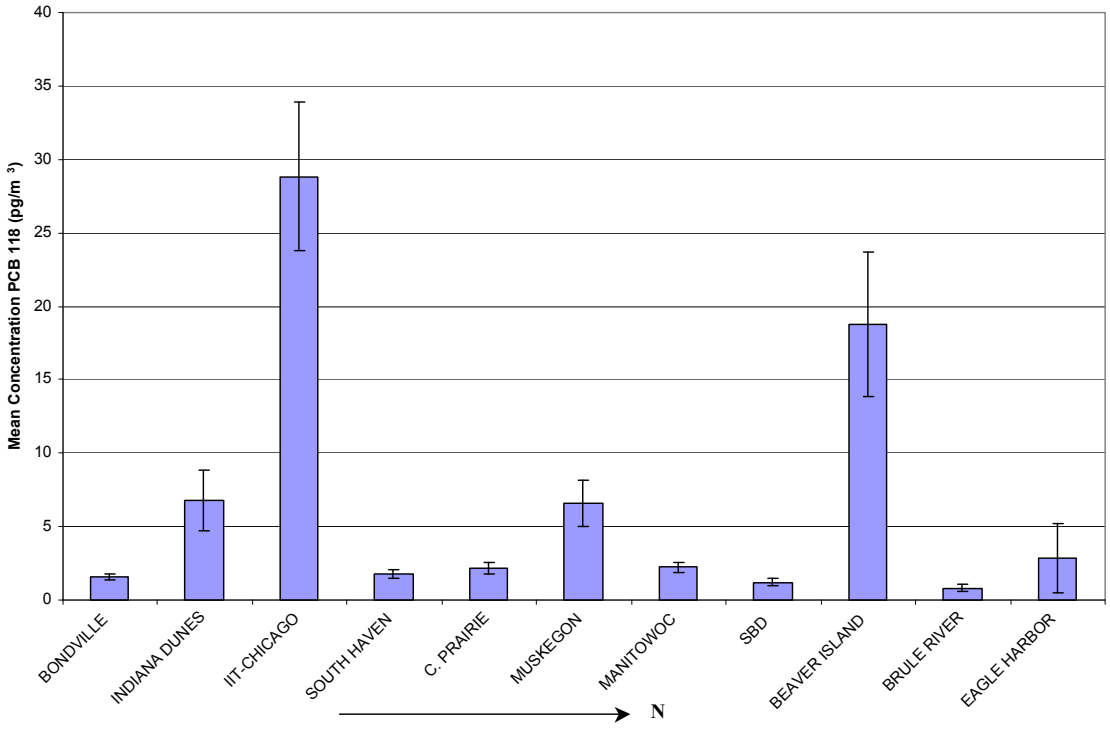
The mean concentration of vapor-phase *trans*-nonachlor at over-water stations was 8.1 pg/m^3, which is lower than the mean concentrations at all other types of stations except the remote stations.

Table 3-8. Mean Monthly Composite Concentrations of Vapor-Phase Total PCBs, PCB 118, and *trans*-Nonachlor at LMMB Study Sampling Stations in and around Lake Michigan from April 1994 to October 1995

Vapor-phase parameter	Sampling Station Type		N	Mean (pg/m^3)	Range (pg/m^3)	RSD (%)
Total PCBs	Shoreline	Urban	19	2600	460 to 6300	72
		Urban-Influenced	75	460	47 to 2000	90
		Rural	19	400	54 to 1400	89
		Remote	34	710	0.0 to 2400	110
		Overall	147	790	0.0 to 6300	140
	Over-water		62	640	4.0 to 4300	160
	Out-of-Basin		42	190	0.0 to 800	93
PCB 118	Shoreline	Urban	19	29	3.5 to 66	77
		Urban-Influenced	75	4.4	0.24 to 33	140
		Rural	19	1.8	0.35 to 5.2	73
		Remote	29	12	0.29 to 70	150
		Overall	142	8.9	0.24 to 70	170
	Over-water		43	13	0.48 to 150	250
	Out-of-Basin		41	1.4	0.075 to 9.9	120
trans-Nonachlor	Shoreline	Urban	19	29	1.5 to 80	77
		Urban-Influenced	75	12	0.0 to 61	100
		Rural	19	10	0.0 to 33	86
		Remote	33	4.6	0.10 to 20	100
		Overall	146	13	0.0 to 80	120
	Over-water		62	8.1	0.0 to 39	110
	Out-of-Basin		41	21	0.0 to 120	150

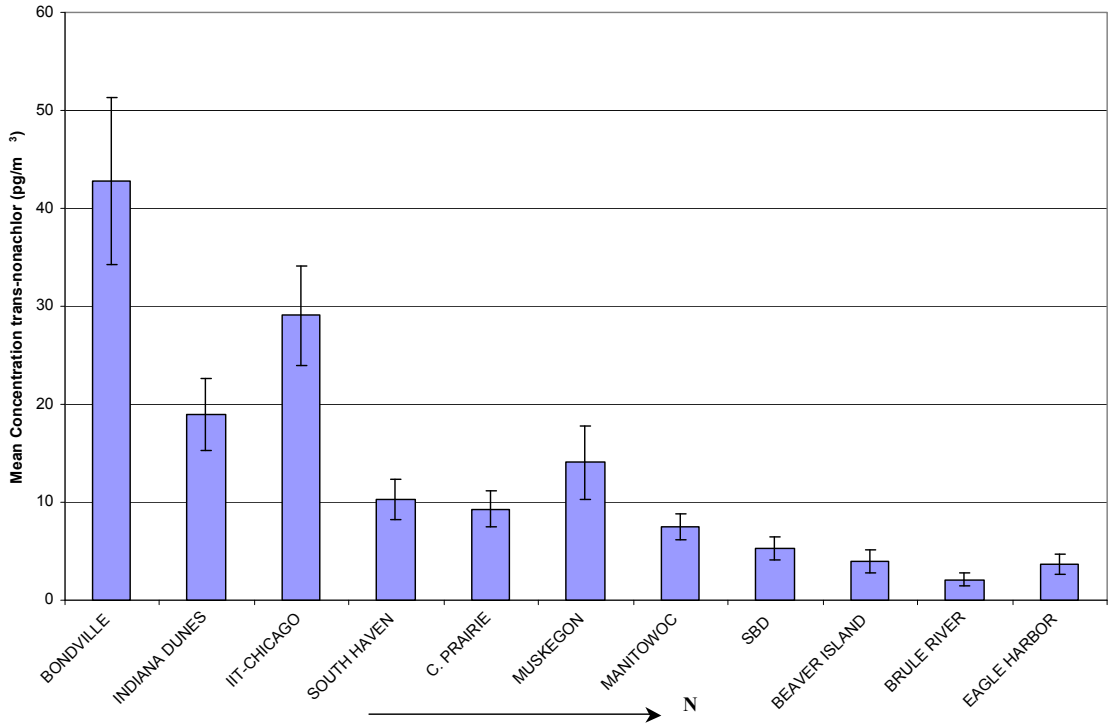
Vapor-phase PCB concentrations varied by station, with the highest mean concentrations generally at the urban IIT Chicago station and the remote Beaver Island station. However, there is no clear trend of concentrations and latitude (Figure 3-4).

Figure 3-4. Vapor-phase PCB 118 Concentrations Measured at Shoreline and Out-of-basin Sampling Stations around Lake Michigan from April 1994 to October 1995



Vapor-phase *trans*-nonachlor concentrations also varied by sampling station. The mean monthly composite sample results for *trans*-nonachlor in Table 3-8 exhibit a general trend of decreasing concentrations from urban stations to remote stations. In addition, the *trans*-nonachlor data exhibit a trend of increasing concentrations moving south across Lake Michigan (Figure 3-5).

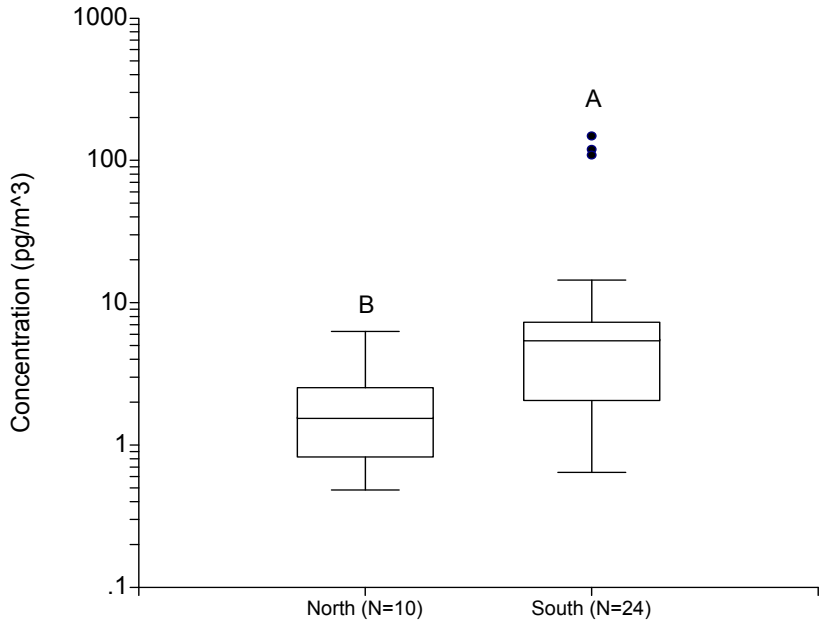
Figure 3-5. Vapor-phase *trans*-Nonachlor Concentrations Measured at Sampling Stations around Lake Michigan from April 1994 to October 1995



Concentrations of vapor-phase PCB congeners in samples collected at over-water sampling locations also differed among stations. Figure 3-6 illustrates a significant difference between sampling stations in Southern Lake Michigan (sites south of 43° latitude) and stations in Northern Lake Michigan (sites north of 43° latitude) for PCB 118. PCB 118 concentrations observed at southern sampling stations were significantly higher than concentrations observed at northern sampling stations.

For vapor-phase *trans*-nonachlor and total PCBs, a significant difference between over-water sampling stations in southern Lake Michigan (sites south of 43° latitude) compared to stations in northern Lake Michigan did *not* occur.

Figure 3-6. Concentrations of PCB 118 in Vapor Measured in Over-water Samples Collected in the Northern and Southern Areas of Lake Michigan



Boxes represent the 25th percentile (bottom of box), 50th percentile (center line), and 75th percentile (top of box) results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. Letters above the boxes represent the results of the analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05). Northern sites are those north of 43° latitude.

3.1.2 Particulate Fraction

Particulate-phase PCB congeners were detected in the majority of the samples collected from all LMMB Study stations. Tables 3-9 to 3-12 present the results for the monthly composite particulate-phase samples from this study. As discussed in Chapter 2, the composite results represent either: 1) the physical compositing of several individual samples collected during a calendar month to create one sample for analysis, or 2) mathematical composites of the results from the analysis of the individual samples collected over a calendar month. In some instances, both physical and mathematical composites were prepared within a month. In these instances, the reported result is a mathematical composite based on both the physical composite samples and the individual samples. The total number of composite results is shown for each station as "N," along with the mean concentration, range, standard deviation, and relative standard deviation (RSD). Tables 3-9 to 3-11 also indicate the percent of the *individual* sample results that were below the sample-specific detection limit, not the percent of the composite results. The mean concentrations were calculated using the results reported by each laboratory (substitution of the detection limit or other value was not used for results below the sample-specific detection limits).

Particulate-phase PCB congener concentrations ranged from 0 pg/m^3 for PCB 180 at the Manitowoc and Sleeping Bear Dunes sampling stations to 8.7 pg/m^3 for PCB 118 at the IIT Chicago sampling station (Tables 3-9 to 3-11). Concentrations of particulate-phase total PCBs ranged from 0 pg/m^3 at the Beaver Island station to 250 pg/m^3 at the IIT Chicago station (Table 3-12). The mean particulate-phase PCB concentrations ranged from 0.10 pg/m^3 for PCB 180 at Sleeping Bear Dunes to 3.2 pg/m^3 at the IIT Chicago station. Mean particulate-phase total PCB concentrations ranged from 0.37 pg/m^3 at over-water Station 6 to 91 pg/m^3 at the IIT Chicago station.

The variability of the PCB concentrations differed among both stations and congeners, with RSD values for PCB 33 ranging from 24% to 77%, from 26% to 190% for PCB 118, and 35% to 210% for PCB 180. In contrast to the vapor-phase results, the greatest RSD values tend to be associated with the stations with larger numbers of samples, while the lowest RSD values occur at the two stations with only four samples, Eagle Harbor and Empire Michigan. However, the low RSD values at these two stations may be due to a lack of seasonal variability since the results for these stations are only from one season. Over-water stations 5 and GB24M have only one sample, therefore, no RSD can be calculated. For stations with greater than 10 samples over the course of the study, the variability for particulate-phase PCB 33 was greatest at IIT Chicago (RSD = 72%) and greatest for PCB 118, PCB 180, and total PCBs at Sleeping Bear Dunes (RSDs of 190%, 210%, and 110%, respectively).

Particulate-phase *trans*-nonachlor was detected much less frequently than PCB congeners in the samples. Except for the samples collected at the Empire Michigan station, *trans*-nonachlor was reported as being below the sample-specific detection limit in 20 to 100% of the particulate-phase samples from the other 16 stations (Table 3-13). Concentrations of particulate-phase *trans*-nonachlor ranged from 0 pg/m^3 at 12 stations to 2.6 pg/m^3 at Bondville. Mean monthly composite concentrations of *trans*-nonachlor for each sampling station ranged from 0.16 pg/m^3 measured at GB24M to 1.2 pg/m^3 measured at IIT Chicago, with a concentration of 1.8 pg/m^3 for the only sample collected at over-water Station 1.

Table 3-9. Monthly Composite Concentrations of Particulate-Phase PCB 33 Measured in Samples Collected Around Lake Michigan from April 1994 to October 1995

Sampling Station		N	Mean (pg/m^3)	Range (pg/m^3)	SD (pg/m^3)	RSD (%)	% Below DL*
Shoreline Atmospheric Stations	Beaver Island	17	0.52	0.21 to 1.4	0.26	50	0
	Chiwaukee Prairie	19	0.52	0.20 to 0.82	0.16	31	0
	IIT Chicago	19	1.7	0.67 to 5.3	1.2	72	0
	Indiana Dunes	19	0.63	0.28 to 1.4	0.29	46	3
	Manitowoc	19	0.43	0.17 to 0.83	0.17	40	5
	Muskegon	16	0.38	0.032 to 0.67	0.19	51	25
	Sleeping Bear Dunes	14	0.59	0.16 to 1.4	0.40	68	7
	South Haven	17	0.58	0.32 to 1.1	0.20	34	11
Out-of-Basin Atmospheric Stations	Bondville	19	0.66	0.24 to 1.1	0.22	33	0
	Brule River	18	0.46	0.18 to 1.0	0.21	47	0
	Eagle Harbor	4	0.32	0.20 to 0.58	0.18	56	0
Over-water Atmospheric Stations	Empire Michigan	4	0.30	0.20 to 0.35	0.071	24	0
	GB24M	1	0.34	NA	NA	NA	100
	5	1	1.3	NA	NA	NA	0

* Value represents the percent of the individual samples collected and analyzed, not of the monthly composite samples prepared from the individual samples.
NA = Not applicable

Table 3-10. Monthly Composite Concentrations of Particulate-phase PCB 118 Measured in Samples Collected Around Lake Michigan from April 1994 to October 1995

Sampling Station		N	Mean (pg/m^3)	Range (pg/m^3)	SD (pg/m^3)	RSD (%)	% Below DL*
Shoreline Atmospheric Stations	Beaver Island	17	1.7	0.51 to 4.0	0.95	56	0
	Chiwaukee Prairie	19	0.47	0.19 to 0.83	0.18	40	0
	IIT Chicago	19	3.2	1.5 to 8.7	1.7	54	0
	Manitowoc	19	0.48	0.20 to 1.3	0.26	54	0
	Muskegon	16	0.67	0.17 to 1.6	0.46	69	0
	Sleeping Bear Dunes	14	0.24	0.023 to 1.8	0.46	190	43
	South Haven	17	0.49	0.20 to 1.9	0.39	80	11
	Indiana Dunes	19	0.77	0.35 to 1.7	0.31	41	0
Out-of-Basin Atmospheric Stations	Bondville	91	0.40	0.19 to 0.89	0.17	44	5
	Brule River	18	0.50	0.14 to 1.4	0.27	53	0
	Eagle Harbor	4	0.22	0.14 to 0.28	0.067	30	0
Over-water Atmospheric Stations	Empire Michigan	4	0.34	0.25 to 0.44	0.089	26	0
	GB24M	1	0.14	NA	NA	NA	100
	5	1	0.61	NA	NA	NA	0
	Spatial Composites	12	0.56	0.065 to 2.0	0.54	96	8

* Value represents the percent of the individual samples collected and analyzed, not of the monthly composite samples prepared from the individual samples.
NA = Not applicable

Table 3-11. Monthly Composite Concentrations of Particulate-Phase PCB 180 Measured in Samples Collected Around Lake Michigan from April 1994 to October 1995

Sampling Station		N	Mean (pg/m^3)	Range (pg/m_3)	SD (pg/m_3)	RSD (%)	% Below DL*
Shoreline Atmospheric Stations	Beaver Island	17	1.0	0.26 to 2.6	0.71	69	0
	Chiwaukee Prairie	19	0.21	0.067 to 0.34	0.075	36	10
	IIT Chicago	19	1.9	0.97 to 4.6	0.84	45	0
	Indiana Dunes	19	0.36	0.10 to 0.71	0.16	45	0
	Manitowoc	19	0.22	0.0 to 0.74	0.15	69	5
	Muskegon	16	0.38	0.14 to 0.83	0.22	59	0
	Sleeping Bear Dunes	14	0.10	0.0 to 0.82	0.21	210	57
	South Haven	17	0.29	0.046 to 1.5	0.34	120	17
Out-of-Basin Atmospheric Stations	Bondville	19	0.26	0.078 to 1.3	0.28	110	14
	Brule River	18	0.18	0.00 to 0.69	0.15	82	6
	Eagle Harbor	4	0.090	0.046 to 0.13	0.034	37	25
Over-Water Atmospheric Stations	Empire Michigan	4	0.11	0.065 to 0.15	0.037	35	0
	GB24M	1	0.11	NA	NA	NA	100
	5	1	0.21	NA	NA	NA	100
	Spatial Composites	12	0.27	0.047 to 0.71	0.20	74	33

* Value represents the percent of the individual samples collected and analyzed, not of the monthly composite samples prepared from the individual samples.
NA = Not applicable

Table 3-12. Monthly Composite Concentrations of Particulate-phase Total PCBs Measured in Samples Collected Around Lake Michigan from April 1994 to October 1995

Sampling Station		N	Mean (pg/m^3)	Range (pg/m^3)	SD (pg/m^3)	RSD (%)
Shoreline Atmospheric Stations	Beaver Island	18	52	0.0 to 110	29	56
	Chiwaukee Prairie	19	22	7.7 to 31	6.1	28
	IIT Chicago	19	91	46 to 250	48	53
	Indiana Dunes	19	33	18 to 66	12	36
	Manitowoc	19	26	8.6 to 110	22	84
	Muskegon	16	24	7.7 to 51	12	49
	Sleeping Bear Dunes	15	18	0.0 to 69	21	110
	South Haven	18	23	0.0 to 47	12	52
Out-of-Basin Atmospheric Stations	Bondville	19	25	9.6 to 58	14	54
	Brule River	18	21	5.8 to 71	14	66
	Eagle Harbor	4	14	8.2 to 20	4.7	33
Over-Water Atmospheric Stations	Spatial Composites	18	19	0.18 to 77	21	110
	Empire Michigan	4	14	8.9 to 18	4.0	29
	GB24M	2	3.9	0.26 to 7.6	5.2	130
	1	1	2.6	NA	NA	NA
	5	3	17	0.25 to 48	27	160
	6	1	0.37	NA	NA	NA

NA = Not applicable

Table 3-13. Monthly Composite Concentrations of Particulate-Phase *trans*-Nonachlor Measured in Samples Collected Around Lake Michigan from April 1994 to October 1995

Sampling Station		N	Mean (pg/m^3)	Range (pg/m^3)	SD (pg/m^3)	RSD (%)	% Below DL*
Shoreline Atmospheric Stations	Beaver Island	17	0.35	0.0 to 0.72	0.22	62	29
	Chiwaukee Prairie	19	0.48	0.0 to 1.0	0.25	53	24
	IIT Chicago	19	1.2	0.0 to 2.5	0.68	58	20
	Indiana Dunes	18	0.64	0.0 to 1.6	0.45	70	34
	Manitowoc	18	0.58	0.075 to 1.4	0.42	73	22
	Muskegon	16	0.47	0.0 to 1.4	0.39	84	31
	Sleeping Bear Dunes	4	0.30	0.0 to 1.1	0.55	190	75
	South Haven	17	0.46	0.0 to 1.2	0.32	71	33
Out-of-Basin Atmospheric Stations	Bondville	19	0.81	0.0 to 2.6	0.89	110	48
	Brule River	18	0.43	0.0 to 1.1	0.31	71	39
	Eagle Harbor	4	0.24	0.051 to 0.49	0.20	84	50
Over-Water Atmospheric Stations	Empire Michigan	4	0.34	0.17 to 0.51	0.14	41	0
	GB24M	2	0.16	0.0 to 0.32	0.23	140	100
	1	1	1.8	NA	NA	NA	0
	5	3	0.36	0.0 to 1.0	0.55	150	67
	6	1	0.74	NA	NA	NA	100
	Spatial Composites	18	0.41	0.0 to 1.6	0.46	110	61

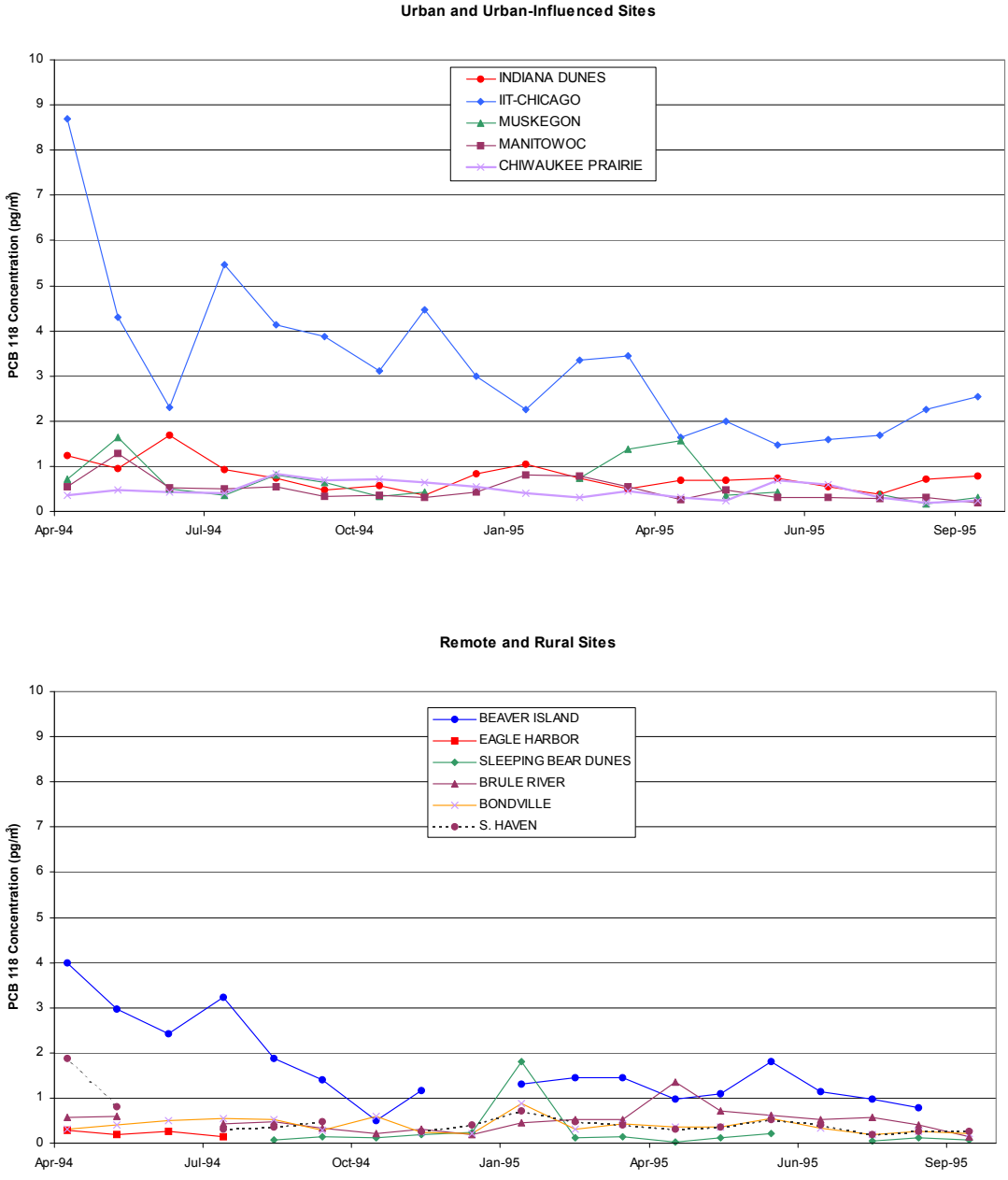
* Value represents the percent of the individual samples collected and analyzed, not of the monthly composite samples prepared from the individual samples.
NA = Not applicable

3.1.2.1 Temporal Variation

Particulate-phase PCB congener and total PCB results exhibited different temporal trends among congeners and also among stations. Season did not have a significant effect on particulate-phase PCB 33 concentrations, but did have a significant effect on particulate-phase total PCBs ($p<0.0001$, two-way ANOVA, PCB concentrations were log-transformed prior to conducting the test). For particulate-phase PCB 118 and PCB 180 concentrations, there was a significant interaction between station and season ($p<0.0361$, two-way ANOVA, PCB concentrations were log-transformed prior to conducting the test). The relationship between season and concentration differed for PCBs 118 and 180 at different stations. Figure 3-7 illustrates the interaction between station and season for PCB 118.

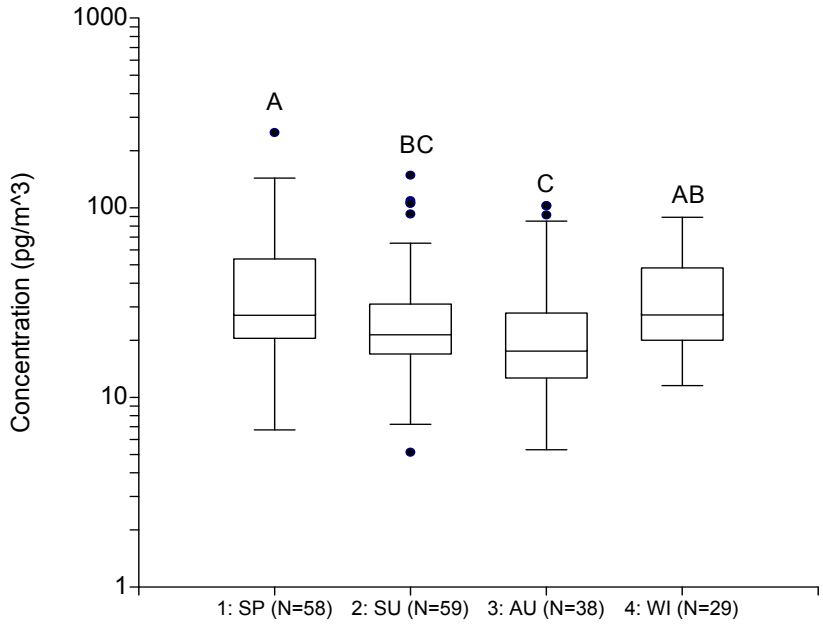
The particulate-phase results for PCB 118 at the Beaver Island and IIT Chicago stations are highest in April 1994 and generally decrease by September 1995, and variable in between. While some of the urban and urban-influenced stations exhibit their highest concentrations of PCB 118 in May 1994 (e.g., Muskegon, Manitowoc, and Indiana Dunes), the overall decrease seen at Beaver Island and IIT Chicago is not apparent at the other stations. The rural and remote stations other than Beaver Island do not show a temporal trend in particulate-phase PCB 118 concentrations. The highest result at Sleeping Bear Dunes occurred in January 1995 (1.8 pg/m^3). However, this result may be due to contamination, as evidenced by the field duplicate composite sample that had a concentration of only 0.19 pg/m^3. The highest result at IIT Chicago in April 1994 is especially striking, given that the other samples collected from this station during April 1995 had lower results than the neighboring months.

Figure 3-7. Temporal Variations in Particulate-phase PCB 118 Concentrations Measured at Lake Michigan Shoreline and Out-of-basin Stations from April 1994 to October 1995



The particulate-phase total PCB concentrations were significantly higher in Spring compared to Autumn and Summer (two-way ANOVA, with Tukey pairwise comparisons) and significantly higher in Winter than Autumn (Figure 3-8).

Figure 3-8. Seasonal Differences in Particulate-phase Total PCB Concentrations Measured at Lake Michigan Shoreline and Out-of-basin Stations from April 1994 to October 1995

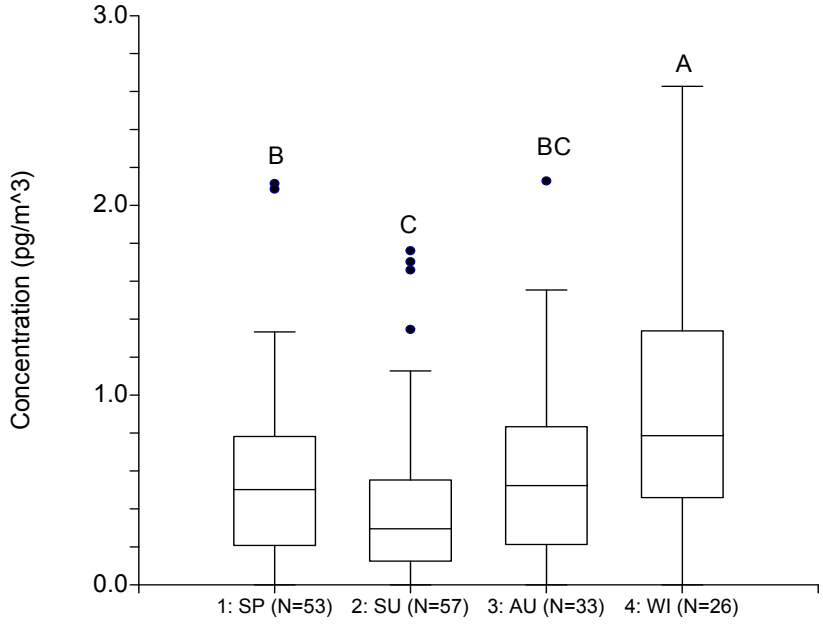


Boxes represent the 25th percentile (bottom of box), 50th percentile (center line), and 75th percentile (top of box) results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. The letters (A - D) above the boxes represent the results of the analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05). Concentration is plotted on a log scale.

The seasonal differences evident in Figure 3-8 were apparent even when the high April 1994 results were removed from the data set. Given that the data were log-transformed before the comparisons, it is not unexpected that removing the April 1994 results did not change the seasonal patterns.

For *trans*-nonachlor, concentrations measured in particulate-phase samples also were significantly different among seasons, with mean concentrations highest in winter and lowest in summer (two-way ANOVA, with Tukey pairwise comparisons, see Figure 3-9). However, the pattern of seasonal differences was not the same as exhibited in the particulate-phase total PCB results.

Figure 3-9. Seasonal Differences in Particulate-phase *trans*-Nonachlor Concentrations Measured at Lake Michigan Shoreline and Out-of-basin Stations from April 1994 to October 1995



Boxes represent the 25th percentile (bottom of box), 50th percentile (center line), and 75th percentile (top of box) results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. The letters (A - D) above the boxes represent the results of the analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05).

Temporal variability could not be evaluated for the over-water stations because of the limited number of composite samples (1 to 4 at any given over-water station) that do not represent either all four seasons in any one year, or the entire time-span of the LMMB Study.

3.1.2.2 Geographical Variation

Particulate-phase PCB congener and total PCB concentrations varied by sampling station (Table 3-14). As was noted for the vapor-phase results, urban and urban-influenced sites had higher mean monthly composite concentrations for the duration of the study period than rural sites, consistent with the hypothesis that urban and urban-influenced areas contain significant sources of particulate-phase PCBs. As also noted for the vapor-phase results, the results for total PCBs and PCB 33 at the remote sites fall between the urban and urban-influenced sites, suggesting the presence of an unknown source for PCBs at the remote sites, likely near Beaver Island (see Figures 3-7 and 3-10).

Table 3-14. Mean Monthly Composite Concentrations of Particulate-phase Total PCBs, PCB 33, and *trans*-Nonachlor at LMMB Study Sampling Stations in and around Lake Michigan between April 1994 and October 1995

Particulate-phase parameter	Sampling Station Type		N	Mean (pg/m^3)	Range (pg/m^3)	RSD(%)
Total PCBs	Shoreline	Urban	19	91	46 to 250	53
		Urban-Influenced	73	26	7.7 to 110	55
		Rural	18	23	0 to 47	52
		Remote	33	37	0 to 110	83
		Overall	143	37	0 to 250	90
	Over-Water		29	16	0.18 to 77	120
	Out-of-Basin		41	22	5.8 to 71	60
PCB 33	Shoreline	Urban	19	1.7	0.67 to 5.3	72
		Urban-Influenced	73	0.50	0.032 to 1.4	46
		Rural	17	0.58	0.32 to 1.1	34
		Remote	31	0.55	0.16 to 1.4	59
		Overall	140	0.68	0.032 to 5.3	93
	Over-Water		18	0.60	0 to 1.6	79
	Out-of-Basin		41	0.54	0.18 to 1.1	45
trans-Nonachlor	Shoreline	Urban	19	1.2	0 to 2.5	58
		Urban Influenced	71	0.54	0 to 1.6	70
		Rural	17	0.46	0 to 1.2	71
		Remote	21	0.34	0 to 1.1	85
		Overall	128	0.59	0 to 2.5	82
	Over-Water		29	0.43	0 to 1.8	110
	Out-of-Basin		41	0.59	0 to 2.6	110

There was no apparent relationship between the particulate-phase concentration of PCB 118 and latitude (see Figure 3-10).

There is an apparent relationship between the particulate-phase concentration of *trans*-nonachlor and latitude (Figure 3-11). Except for the high mean particulate-phase concentration observed at the urban IIT Chicago site, the mean concentration of *trans*-nonachlor generally decreases moving from south to north across Lake Michigan.

Figure 3-10. Particulate-phase PCB 118 Concentrations Measured at Lake Michigan Shoreline and Out-of basin Stations from April 1994 to October 1995

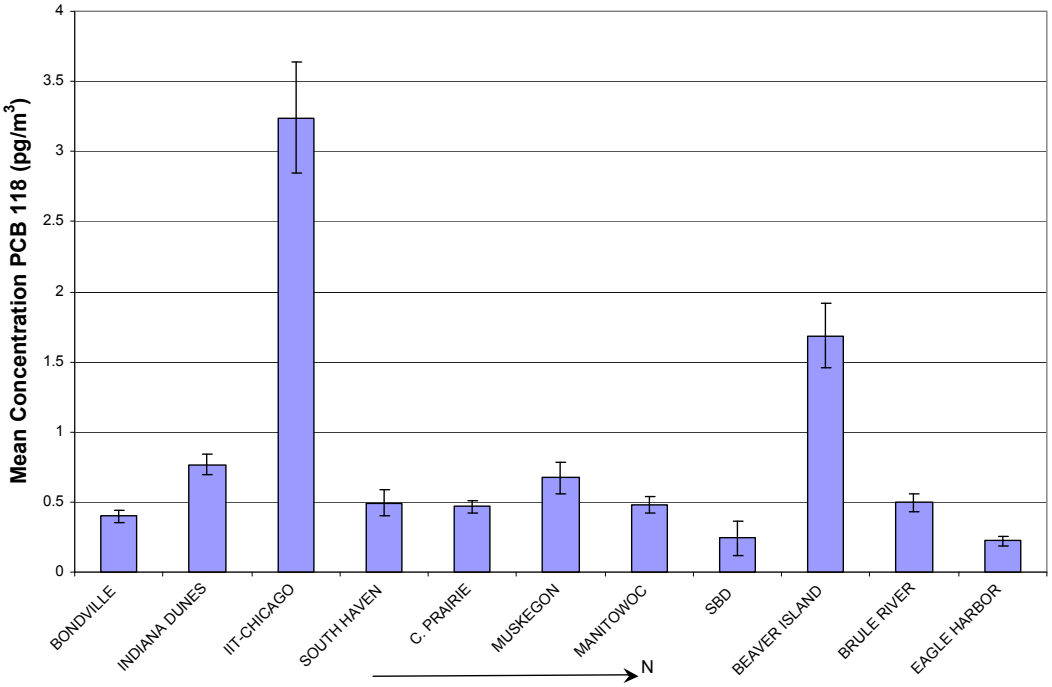
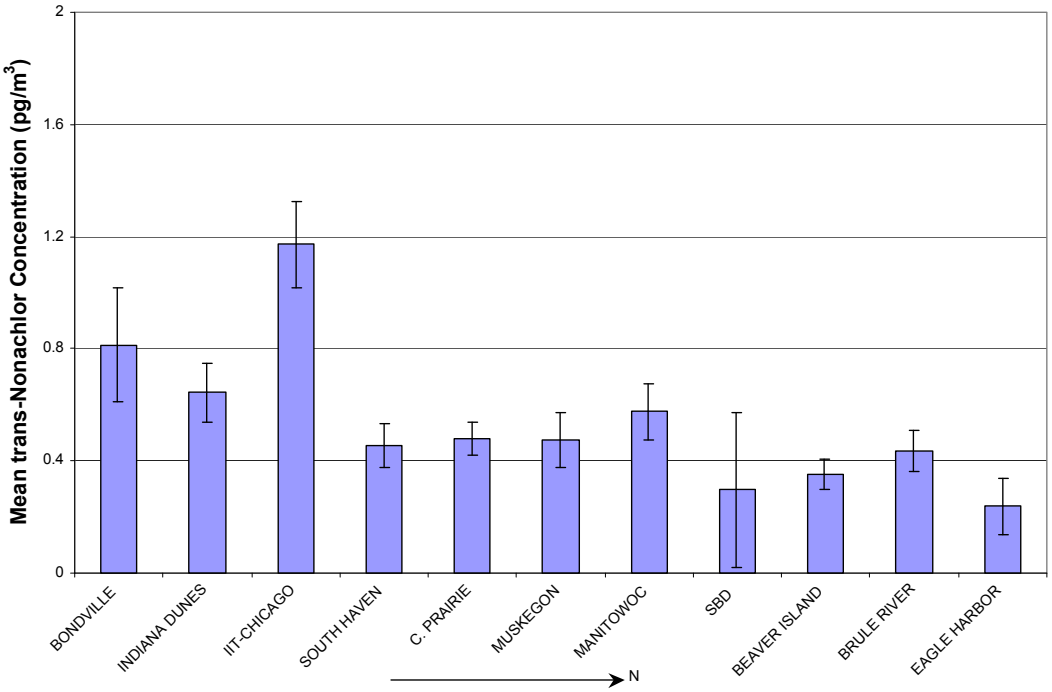


Figure 3-11. Particulate-phase *trans*-Nonachlor Concentrations Measured at Lake Michigan Shoreline and Out-of-basin Stations from April 1994 to October 1995



3.1.3 Precipitation Fraction

PCB congeners were detected in many of the precipitation samples collected from the LMMB Study stations. However, the overall frequency of occurrence of PCBs in the precipitation samples was lower than for the vapor-phase and particulate-phase samples. The frequency of precipitation samples with results below the sample-specific detection limit was greatest for PCB 33 compared to either PCB 118 or 180.

The precipitation samples were collected as described in Chapter 2. The samples collected from the shoreline and out-of-basin stations represent true 28-day composite samples. The precipitation samples collected from the over-water stations represent single-day composite results. Tables 3-15 to 3-18 present the results for the composite precipitation samples from this study. The total number of composite results is shown for each station as "N," along with the mean concentration, range, standard deviation, relative standard deviation (RSD), and the percent of the sample results that were below the sample-specific detection limit. In calculating these summary statistics, the analytical results for each sample were volume-weighted to account for differences in the total volume of precipitation that fell during each 28-day period. The mean concentrations were calculated using the results reported by each laboratory (substitution of the detection limit or other value was not used for results below the sample-specific detection limits).

Precipitation PCB concentrations ranged from 0 pg/L for PCB 33 at 10 of the 12 shoreline and out-of-basin sampling stations (see Table 3-15) to 5,500 pg/L for PCB 118 at Muskegon (Table 3-16). Mean precipitation PCB concentrations ranged from 2.2 pg/L for PCB 33 at the Empire Michigan station to 470 pg/L for PCB 33 at the IIT Chicago station. For total PCBs, the mean concentrations in precipitation ranged from 290 pg/L at the Eagle Harbor station to 16,000 pg/L at the IIT Chicago station. The precipitation samples collected at the IIT Chicago site had the highest volume-weighted mean concentrations of PCBs 33, 180, and total PCBs, while PCB 118 had highest volume-weighted mean concentration at the Muskegon site (see Tables 3-15 to 3-18).

Many of the summary statistics for the precipitation samples collected from the over-water stations could not be calculated because only one precipitation sample was collected at most of these stations.

trans-Nonachlor was detected even less frequently than the PCB congeners in the precipitation samples (Table 3-19). Except for the samples collected at the IIT Chicago station, *trans*-nonachlor was reported as being below the sample-specific detection limit in 75 to 100% of the precipitation samples from all stations. The concentrations of *trans*-nonachlor in the precipitation samples ranged from 0 pg/L at every site to a high of 630 pg/L at the Chiwaukee Prairie site. The mean concentrations of *trans*-nonachlor in precipitation samples ranged from 0 pg/L at three over-water stations to 120 pg/L at the IIT Chicago station. Similarly, the volume-weighted mean concentrations ranged from 0 pg/L at three over-water stations to 100 pg/L at the IIT Chicago site.

As with the PCB results, many of the summary statistics for the precipitation samples collected from the over-water station could not be calculated because only one precipitation sample was collected at most of these stations.

Table 3-15. Monthly Composite Concentrations of PCB 33 Measured in Precipitation Samples Collected around Lake Michigan from April 1994 to October 1995

Sampling Station		N	VW Mean (pg/L)	Mean (pg/L)	Range (pg/L)	SD (pg/L)	RSD (%)	% Below DL
Shoreline Atmospheric Stations	Beaver Island	19	45	42	0.0 to 450	100	240	68
	Chiwaukee Prairie	17	18	19	0.0 to 83	26	130	59
	IIT Chicago	16	270	470	15 to 3200	800	170	6
	Indiana Dunes	20	39	38	0.0 to 160	38	100	50
	Manitowoc	18	36	51	0.0 to 350	85	170	50
	Muskegon	18	37	67	0.0 to 470	120	180	50
	Sleeping Bear Dunes	14	58	83	13 to 300	72	86	7
	South Haven	19	47	74	0.0 to 620	150	210	47
Out-of-basin Atmospheric Stations	Bondville	20	45	71	0.0 to 310	84	120	30
	Brule River	18	15	32	0.0 to 310	78	240	72
	Eagle Harbor	3	21	16	0.0 to 47	27	170	67
Over-water Atmospheric Stations	Empire Michigan	4	3.0	2.2	0.0 to 8.8	4.4	200	100
	GB17	1	33	33	NA	NA	NA	100
	GB24M	1	10	10	NA	NA	NA	100
	1	1	6.9	6.9	NA	NA	NA	100
	5	1	36	36	NA	NA	NA	100
	23M	1	7.6	7.6	NA	NA	NA	100
	380	1	8.5	8.5	NA	NA	NA	100

NA = Not applicable

Table 3-16. Monthly Composite Concentrations of PCB 118 Measured in Precipitation Samples Collected around Lake Michigan from April 1994 to October 1995

Sampling Station		N	VW Mean (pg/L)	Mean (pg/L)	Range (pg/L)	SD (pg/L)	RSD (%)	% Below DL
Shoreline Atmospheric Stations	Beaver Island	19	41	53	5.5 to 250	67	130	11
	Chiwaukee Prairie	16	26	38	10 to 79	23	61	13
	IIT Chicago	16	230	440	48 to 2300	710	160	0
	Indiana Dunes	20	34	41	8.2 to 230	48	120	0
	Manitowoc	17	46	81	6.3 to 880	210	250	18
	Muskegon	17	240	360	13 to 5500	1300	360	0
	Sleeping Bear Dunes	14	11	16	3.4 to 37	9.7	59	50
	South Haven	19	35	110	6.2 to 1600	350	320	5
Out-of-basin Atmospheric Stations	Bondville	20	24	34	11 to 93	25	74	0
	Brule River	18	67	61	0.0 to 770	180	290	39
	Eagle Harbor	3	5.8	4.9	0.0 to 11	5.8	120	67
Over-water Atmospheric Stations	Empire Michigan	3	7.7	5.7	0.0 to 17	9.9	170	67
	GB17	1	76	76	NA	NA	NA	0
	GB24M	1	23	23	NA	NA	NA	0
	1	1	27	27	NA	NA	NA	0
	5	1	45	45	NA	NA	NA	100
	23M	1	12	12	NA	NA	NA	0
	380	1	17	17	NA	NA	NA	0

NA = Not applicable

Table 3-17. Monthly Composite Concentrations of PCB 180 Measured in Precipitation Samples Collected around Lake Michigan from April 1994 to October 1995

Sampling Station		N	VW Mean (pg/L)	Mean (pg/L)	Range (pg/L)	SD (pg/L)	RSD (%)	% Below DL
Shoreline Atmospheric Stations	Beaver Island	19	23	33	2.5 to 160	42	130	21
	Chiwaukee Prairie	17	24	41	7.8 to 150	39	95	18
	IIT Chicago	16	180	320	14 to 1900	520	160	0
	Indiana Dunes	20	30	38	4.6 to 210	47	120	10
	Manitowoc	18	16	35	0.0 to 210	53	150	33
	Muskegon	18	22	25	0.0 to 50	12	48	17
	Sleeping Bear Dunes	14	5.5	7.7	0.0 to 17	6.3	82	93
	South Haven	19	18	37	5.6 to 370	81	220	32
Out-of-basin Atmospheric Stations	Bondville	20	12	18	0.0 to 80	18	100	40
	Brule River	18	12	14	0.0 to 45	13	93	50
	Eagle Harbor	3	2.5	3.2	0.0 to 7.4	3.8	120	100
Over-water Atmospheric Stations	Empire Michigan	4	9.2	11	2.2 to 20	8.1	73	75
	GB17	1	29	29	NA	NA	NA	100
	GB24M	1	8.5	8.5	NA	NA	NA	100
	1	1	14	14	NA	NA	NA	0
	5	1	19	19	NA	NA	NA	100
	23M	1	3.5	3.5	NA	NA	NA	100
	380	1	6.9	6.9	NA	NA	NA	100

NA = Not applicable

Table 3-18. Monthly Composite Concentrations of total PCBs Measured in Precipitation Samples Collected around Lake Michigan from April 1994 to October 1995

Sampling Station		N	Mean (pg/L)	Range (pg/L)	SD (pg/L)	RSD (%)
Shoreline Atmospheric Stations	Beaver Island	20	1900	0.0 to 11000	2800	150
	Chiwaukee Prairie	20	1800	0.0 to 4700	1200	66
	IIT Chicago	17	16000	0.0 to 110000	28000	180
	Indiana Dunes	21	1500	0.0 to 7200	1500	100
	Manitowoc	20	2600	0.0 to 18000	4200	160
	Muskegon	20	2600	0.0 to 19000	4000	150
	Sleeping Bear Dunes	16	1300	0.0 to 2800	880	66
	South Haven	21	3800	0.0 to 48000	10000	280
Out-of-basin Atmospheric Stations	Bondville	21	1700	0.0 to 4200	1100	69
	Brule River	19	1700	0.0 to 13000	2900	170
	Eagle Harbor	4	290	0.0 to 700	300	100
Over-water Atmospheric Stations	Empire Michigan	4	2000	520 to 4800	2000	100
	GB17	1	2300	NA	NA	NA
	GB24M	1	680	NA	NA	NA
	1	1	750	NA	NA	NA
	5	1	1500	NA	NA	NA
	23M	1	360	NA	NA	NA
	380	1	510	NA	NA	NA

NA = Not applicable

Table 3-19. Monthly Composite Concentrations of *trans*-Nonachlor Measured in Precipitation Samples Collected around Lake Michigan from April 1994 to October 1995

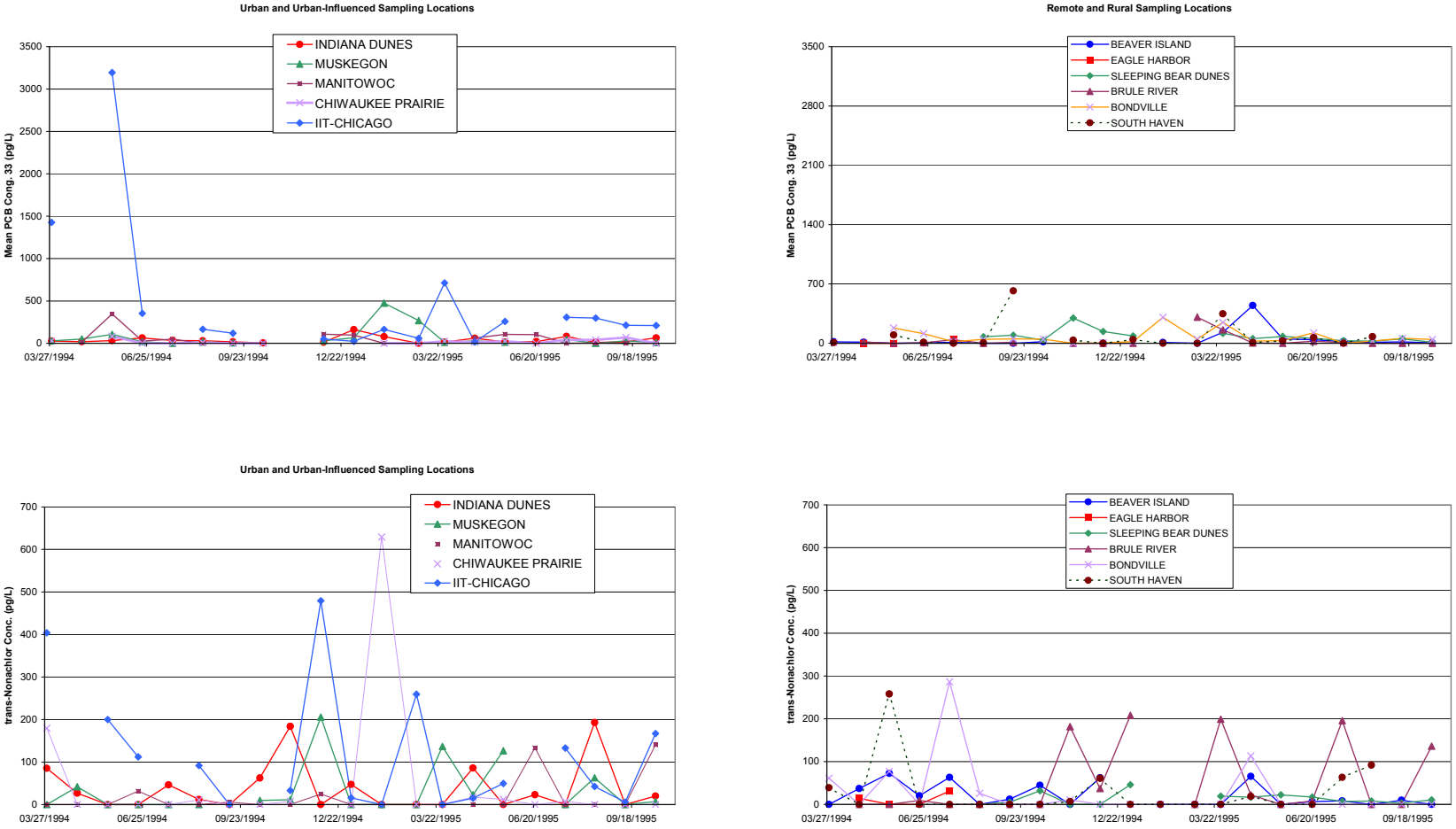
Sampling Station		N	VW Mean (pg/L)	Mean (pg/L)	Range (pg/L)	SD (pg/L)	RSD (%)	% Below DL
Shoreline Atmospheric Stations	Beaver Island	20	18	20	0.0 to 73	27	130	80
	Chiwaukee Prairie	20	11	43	0.0 to 630	140	330	90
	IIT Chicago	17	100	120	0.0 to 480	140	120	41
	Indiana Dunes	21	26	37	0.0 to 190	58	150	76
	Manitowoc	20	17	17	0.0 to 140	42	250	90
	Muskegon	19	27	33	0.0 to 210	59	180	79
	Sleeping Bear Dunes	14	12	13	0.0 to 46	13	100	100
	South Haven	21	13	26	0.0 to 260	59	230	76
Out-of-basin Atmospheric Stations	Bondville	21	29	27	0.0 to 290	67	250	76
	Brule River	19	37	53	0.0 to 210	82	160	79
	Eagle Harbor	4	14	11	0.0 to 31	15	130	75
Over-water Atmospheric Stations	Empire Michigan	4	16	39	0.0 to 130	62	160	100
	GB17	1	0.0	0.0	NA	NA	NA	100
	GB24M	1	0.0	0.0	NA	NA	NA	100
	1	1	20	20	NA	NA	NA	100
	5	1	69	69	NA	NA	NA	100
	23M	1	13	13	NA	NA	NA	100
	380	1	0.0	0.0	NA	NA	NA	100

NA = Not applicable

3.1.3.1 Temporal Variation

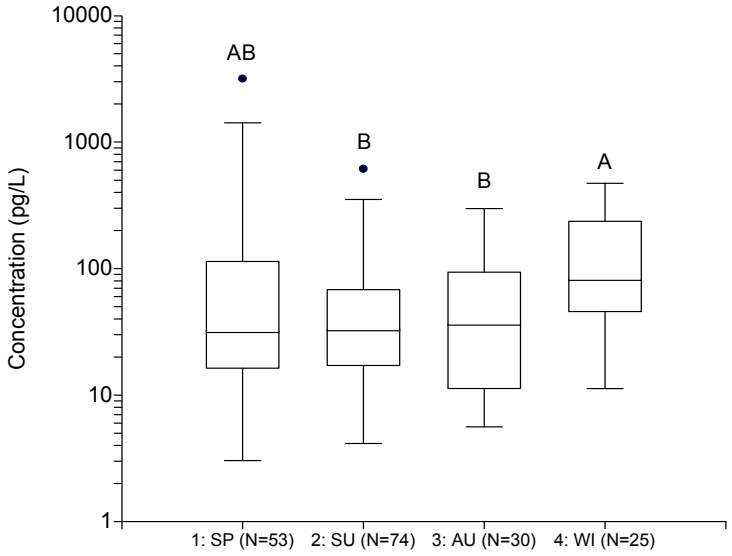
The PCB congeners and total PCBs exhibited no clear temporal trends in the precipitation samples collected at any of the stations. Figure 3-12 presents the results for PCB 33 and *trans*-nonachlor over the course of the LMMB Study, by station, differentiating the urban and urban-influenced stations from the rural and remote stations. The results for PCB 33 at the IIT Chicago site in May 1994 are 5 - 10 times higher than any other result for this congener throughout the study. Although there are several results for *trans*-nonachlor that are higher than those from the IIT Chicago site in May 1994, the results for *trans*-nonachlor exhibit the same sharp decline from May 1994 to June 1994 as was seen for the PCB 33 results at the same site.

Figure 3-12. Temporal Variation in Precipitation PCB 33 (top) and *trans*-Nonachlor (bottom) Concentrations Measured at Lake Michigan Shoreline and Out-of-basin Stations from March 1994 to October 1995



There is a significant difference in the concentrations of PCB 33 in precipitation among seasons (p=0.0248, ANOVA, with Tukey pairwise comparisons) (Figure 3-13). Concentrations are significantly higher in winter than in summer and autumn. The variability during all four seasons is large enough that there is considerable overlap in the box plots.

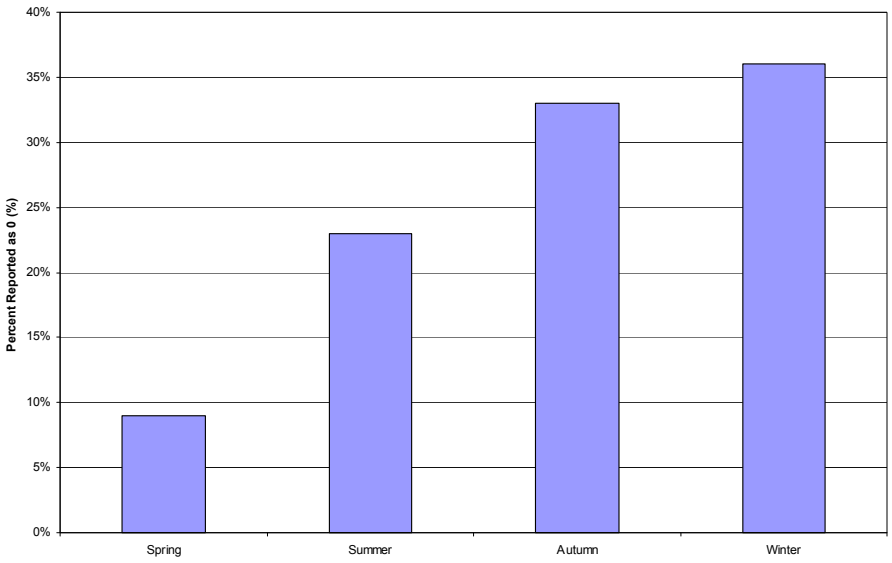
Figure 3-13. Seasonal Patterns of PCB 33 Concentrations in Precipitation Measured at Lake Michigan Shoreline and Out-of-basin Stations from March 1994 to October 1995



Boxes represent the 25th percentile (bottom of box), 50th percentile (center line), and 75th percentile (top of box) results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. The letters (A - D) above the boxes represent the results of the analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05). Concentration is plotted on a log scale.

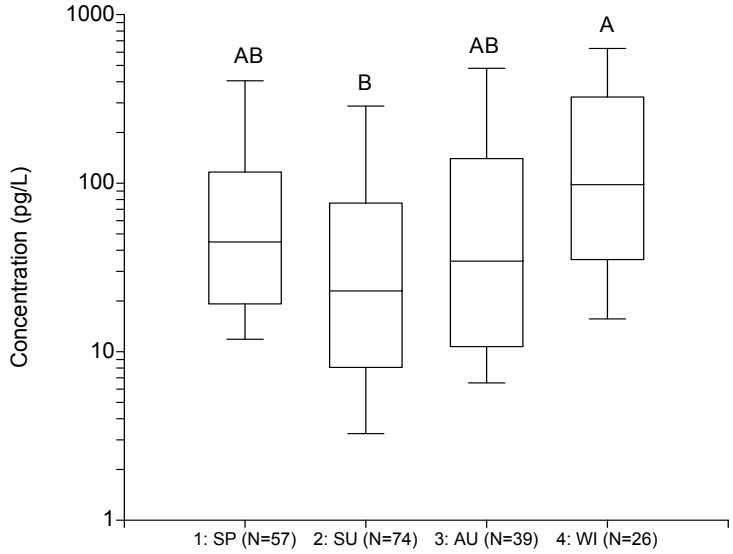
Additionally, there is difference for the seasons in the percentage of samples with results for PCB 33 reported as zero (Figure 3-14). There is a clear and substantial increase in the percent of such samples from spring to winter. These differences were significant based on a Chi-square test at alpha-0.05 (p=0.0201). This is notable, given that the concentration of PCB 33 is significantly higher in winter than summer and autumn, even though more winter samples were reported as zero.

Figure 3-14. Percent of Precipitation PCB 33 Sample Results Reported as Zero, by Season



The concentrations of *trans*-nonachlor also showed a significant difference among seasons (Figure 3-15). The winter concentrations of *trans*-nonachlor are significantly higher than the summer concentrations. Spring and Autumn concentrations are not significantly different from one another, or from either winter or summer.

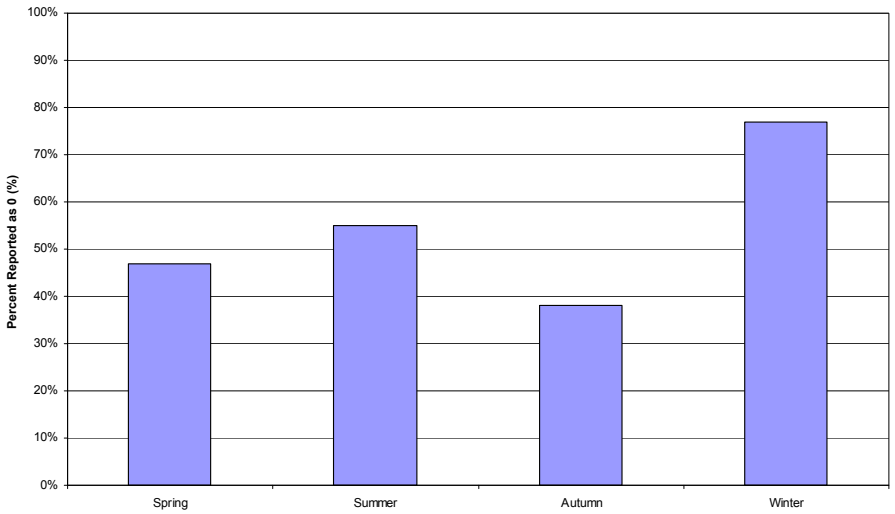
Figure 3-15. Seasonal Patterns of *trans*-Nonachlor Concentrations in Precipitation Measured at Lake Michigan Shoreline and Out-of-basin Stations from March 1994 to October 1995



Boxes represent the 25th percentile (bottom of box), 50th percentile (center line), and 75th percentile (top of box) results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. The letters (A - D) above the boxes represent the results of the analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05). Concentration is plotted on a log scale.

The overall percentage of samples reported as zero for *trans*-nonachlor is much higher than for PCB 33. Figure 3-16 shows the relationship with season, which is not as clear as for PCB 33. These differences were significant, based on a Chi-square test at alpha=0.05 (p=0.0173).

Figure 3-16. Percent of Precipitation *trans*-Nonachlor Sample Results Reported as Zero, by Season



3.1.3.2 Geographical Variation

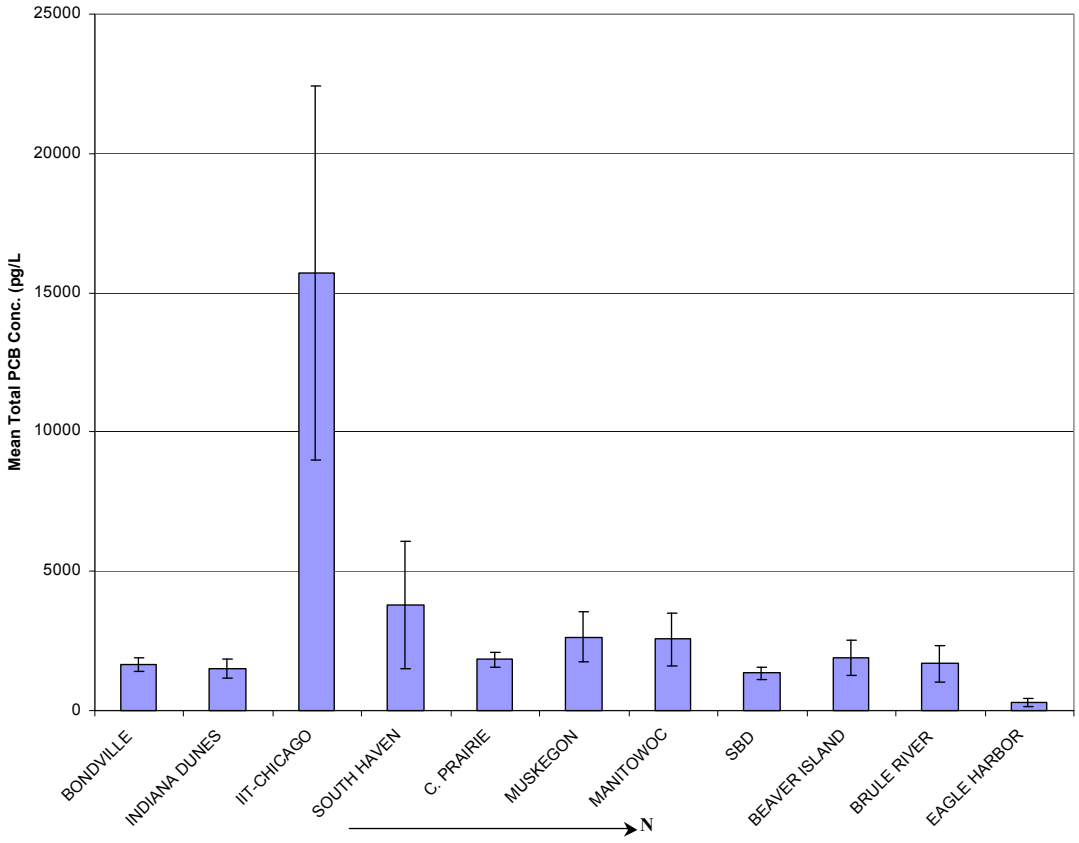
Precipitation PCB congener and total PCB concentrations varied by sampling station. Table 3-20 provides the mean composite sample concentration, the range, and the RSD, for the precipitation samples collected in the LMMB Study. The urban and urban-influenced sites had higher mean monthly composite concentrations for the duration of the study period than remote sites, consistent with the hypothesis that urban and urban-influenced areas contain significant sources of PCBs. However, the mean results for total PCBs and PCB 33 in the precipitation samples from the rural sites are higher than those for both the remote and the urban-influenced sites. The results for precipitation differ from those for the vapor-phase and particulate-phase, where the remote sites showed higher than anticipated concentrations of PCBs, suggesting that the unknown source near the Beaver Island site did not have an effect on PCB concentrations in precipitation.

Table 3-20. Mean Precipitation Concentrations of Total PCB, PCB 33 and *trans*-Nonachlor at LMMB Study Sampling Stations in and around Lake Michigan between March 1994 and October 1995

Precipitation Parameter	Sampling Station Type		N	Mean (pg/L)	Range (pg/L)	RSD (%)
Total PCBs	Shoreline	Urban	17	15800	0.0 to 110,000	180
		Urban-influenced	81	2100	0.0 to 19,000	140
		Rural	21	3800	0.0 to 48,000	280
		Remote	36	1600	0.0 to 11,000	130
		Overall	155	3700	0.0 to 110,000	290
	Over-water		10	1400	361 to 4,800	100
	Out-of-basin		44	1500	0.0 to 13,000	130
PCB 33	Shoreline	Urban	16	470	15 to 3,200	170
		Urban-influenced	73	44	0.0 to 4,700	170
		Rural	19	74	0 to 620	210
		Remote	33	60	0.0 to 450	150
		Overall	141	100	0.0 to 3,200	310
	Over-water		10	11	0.0 to 36	120
	Out-of-basin		41	50	0.0 to 310	160
trans-Nonachlor	Shoreline	Urban	17	120	0.0 to 480	120
		Urban-influenced	80	33	0.0 to 630	260
		Rural	21	26	0.0 to 260	230
		Remote	34	17	0.0 to 73	130
		Overall	152	38	0.0 to 630	230
	Over-water		10	26	0.0 to 130	170
	Out-of-basin		44	37	0.0 to 290	200

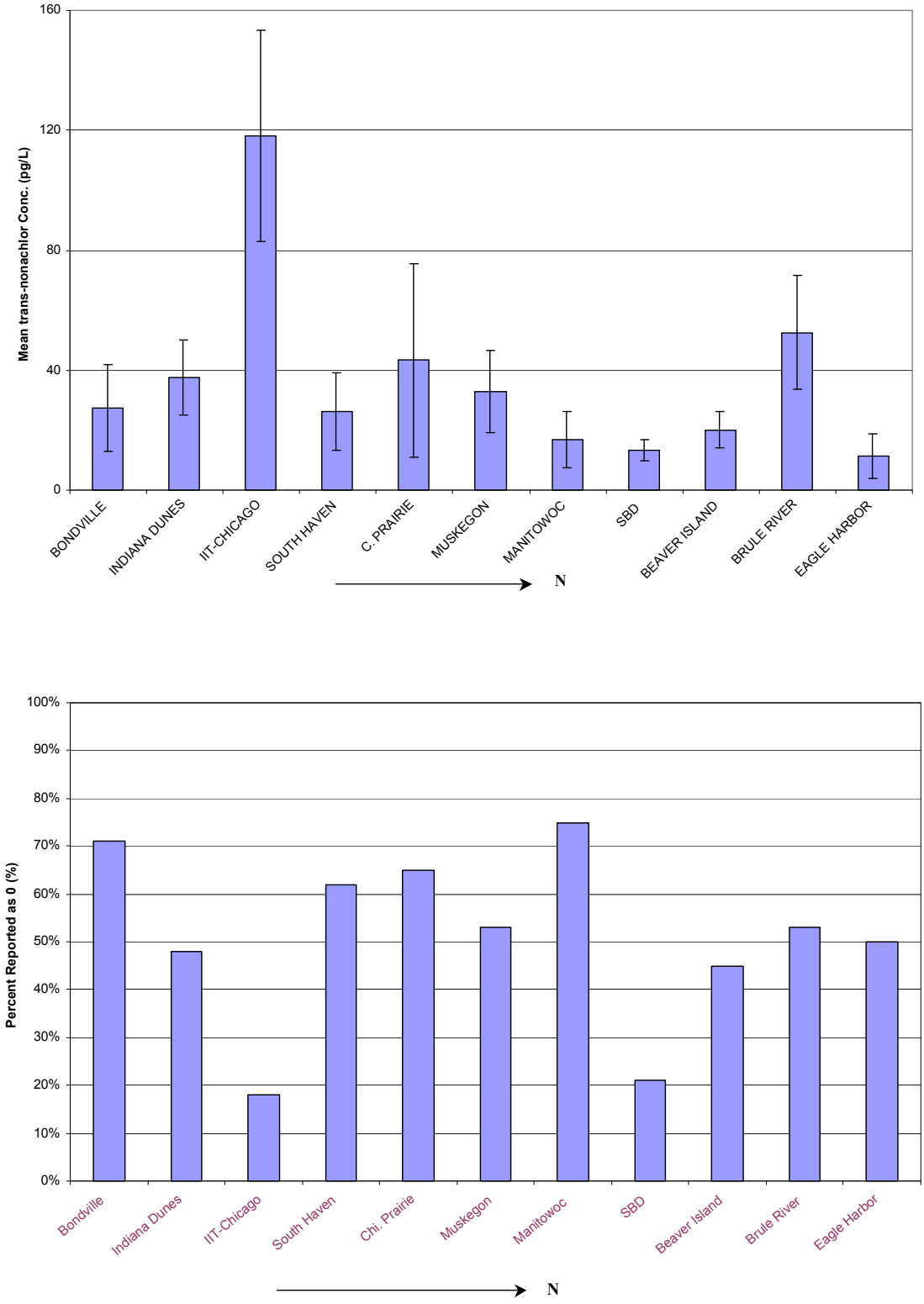
Although there is a general decrease in precipitation total PCB concentrations moving north from the high concentrations observed at the IIT Chicago site, the variability in the data for the stations does not reveal a clear trend (Figure 3-17).

Figure 3-17. Precipitation-phase Total PCB Concentrations Measured at Lake Michigan Shoreline and Out-of-basin Stations from March 1994 to October 1995



The top portion of Figure 3-18 is a similar plot of *trans*-nonachlor concentrations in precipitation by station. Again, aside from the general decrease in the concentrations north of the IIT Chicago site, there is not a prominent trend by latitude. The bottom portion of Figure 3-18 presents the percentage of precipitation samples in which *trans*-nonachlor was reported as zero. In general, the sites with lower mean concentrations of *trans*-nonachlor in precipitation had higher percentages of sample reported as zero. Conversely, the IIT Chicago site had the highest mean concentration in precipitation and the lowest percentage of results reported as zero. The Sleeping Bear Dunes site also had a low percentage of results reported as zero, although it had one of the lowest mean concentrations in this study.

Figure 3-18. Precipitation-phase *trans*-Nonachlor Concentrations Measured at Lake Michigan Shoreline and Out-of-basin Stations from March 1994 to October 1995 (top) and the Percent of Sample Results Reported as Zero for each Sampling Location (bottom)



3.1.4 Dry Deposition

Dry deposition samples were collected from a limited number of sites during the LMMB Study using the procedures described in Chapter 2. The frequencies of occurrence of the PCB congeners varied greatly. Table 3-21 presents the results for the dry deposition samples from this study. The total number of samples is shown for each station as "N," along with the mean concentration, range, standard deviation, and relative standard deviation (RSD). The mean concentrations were calculated using the results reported by each laboratory (substitution of the detection limit or other value was not used for results below the sample-specific detection limits).

Note that the units for the dry deposition samples differ significantly from those for the vapor-phase and particulate-phase samples. Based on the manner in which the samples are collected, dry deposition results are reported here in terms of mass per unit area, in ng/m^2, not the mass per unit volume units of pg/m^3 used for the other phases. Also, PCB 33 was not measured in the dry deposition samples.

Dry-deposition PCB congener concentrations ranged from 140 ng/m^2 for PCB 118 at the IIT Chicago sampling station to over 3 million ng/m^2 for PCB 180 at the South Haven sampling station. Total PCBs in the dry deposition samples exhibited a similar range. Mean concentrations for PCBs in dry deposition ranged from 450 ng/m^2 at the IIT Chicago station to 1.5 million ng/m^2 at the South Haven station. Mean concentration for dry deposition total PCBs ranged from 1800 ng/m^2 at the Chicago SWFP crib intake to 320,000 ng/m^2 at the South Haven station.

The analysis of the dry deposition samples presented more difficulties than the other phases studied. As a result, a larger proportion of data for the dry deposition samples were qualified or found invalid, thereby complicating the summary statistics shown in Table 3-21. In some cases, only one sample had valid results for a specific PCB congener, such that a range and standard deviation could not be determined. In addition the very high concentrations of PCB 180 observed in a few samples at the South Haven station significantly skew the mean, range, and standard deviations reported in Table 3-21 for this congener and for the total PCBs.

The frequencies at which the PCB congeners were found above the sample-specific detection limits also varied greatly by congener. PCB 118 was found below the detection limit in 33 to 100% of the dry deposition samples, while there were fewer valid results for PCB 180 above the detection limit (Table 3-21).

trans-Nonachlor was reported in many of the dry deposition samples, but generally at lower concentrations than the PCBs (Table 3-21). The concentration of *trans*-nonachlor in dry deposition samples ranged from 0 ng/m^2 at South Haven to 209 ng/m^2 at the Chicago SWFP Crib Intake. Most of the results for *trans*-nonachlor were reported as being below the sample-specific detection limits (e.g., 60 to 100%).

Table 3-21. Monthly Composite Concentrations of PCBs and *trans*-Nonachlor Measured in Dry Deposition

Parameter	Sampling Station	N	Mean (ng/m^2)	Range (ng/m^2)	SD (ng/m^2)	RSD (%)	% Below DL
PCB 118	Chicago SWFP Crib Intake	2	604	534 to 674	99.0	16	50
	IIT Chicago	7	453	144 to 919	296	65	100
	Sleeping Bear Dunes	3	745	524 to 1160	360	48	33
PCB 180	IIT Chicago	1	3220	NA	NA	NA	0
	Sleeping Bear Dunes	1	884	NA	NA	NA	0
	South Haven	2	1,580,000	5240 to 3,160,000	2,230,000	141	0
Total PCBs	Chicago SWFP Crib Intake	9	1830	324 to 5150	1710	94	NC
	Harrison Crib	1	5400	NA	NA	NA	NC
	IIT Chicago	13	7060	1720 to 23,500	6480	92	NC
	Sleeping Bear Dunes	8	6120	48.6 to 19,600	7940	130	NC
	South Haven	11	315,000	109 to 3,380,000	1,020,000	323	NC
trans-Nonachlor	Chicago SWFP Crib Intake	9	78.2	34.8 to 209	52.0	66	89
	IIT Chicago	5	64.8	0.00 to 100	40.6	63	60
	Sleeping Bear Dunes	3	39.4	18.2 to 55.2	19.1	48	100
	South Haven	4	25.7	0.00 to 58.5	30.0	118	75

NA = Not applicable. Only one result was reported.
NC = Not calculated. The total PCB concentration is the sum of the results for the individual PCB congeners, each of which has a sample-specific detection limit. However, detection limits are not additive, so there is no meaningful way to specify a detection limit for total PCBs.

3.2 Quality Implementation and Assessment

As described in Section 1.5.5, the LMMB QA program prescribed minimum standards to which all organizations collecting data were required to adhere. The quality activities implemented for the PCBs and *trans*-nonachlor monitoring portion of the study are further described in Section 2.7 and included use of SOPs, training of laboratory and field personnel, and establishment of MQOs for study data. A detailed description of the LMMB quality assurance program is provided in the Lake Michigan Mass Balance Study Quality Assurance Report (USEPA, 2001b). A brief summary of data quality issues for the atmospheric PCBs and *trans*-nonachlor data is provided below.

As discussed in Section 2.5, because data comparability was important to the successful development of the mass balance model, the PIs used similar sample collection, extraction, and analysis methods for the PCB and *trans*-nonachlor monitoring in this study. For a small portion of the study (June 15, 1994 to September 22, 1994), a revision to the silica gel clean-up procedure for the determination of PCBs in precipitation and particulate phases resulted in coelution of PCB 99 with *trans*-nonachlor. Affected sample results are qualified with the high bias flag (HIB) in the database.

The PIs used surrogate spikes to monitor the bias of the analytical procedure. Analytical results for PCBs in vapor, precipitation, and particulate phases were corrected for surrogate recoveries. Analytical results for PCBs in dry deposition were *not* corrected for surrogate recoveries because the recoveries of the surrogates (PCB 14 and PCB 65) were subject to chromatographic interferences. The PI noted that the recoveries were too erratic to be used as reliable indicators of method accuracy. Sample results for PCBs

associated with surrogate recoveries outside the MQO limits were qualified with the failed surrogate spike flag (FSS).

Analytical results for *trans*-nonachlor were not corrected for surrogate recoveries, except for those collected and analyzed by Indiana University (Sleeping Bear Dunes site August 1994 to October 1995. Analytical results were considered invalid (INV) and qualified when surrogate recoveries were less than 10%. Some PCB data were found to be invalid for this reason, but the *trans*-nonachlor surrogate recoveries were never below 10%.

Laboratory matrix spike samples also were used to monitor the bias of the analytical procedure. For the dry deposition analyses, a spiked laboratory solvent blank also was prepared and analyzed. Analytical results associated with matrix spike samples with recoveries below the MQO limits were qualified with the failed matrix spike and low bias flags (FMS and LOB) and results associated with matrix spike samples with recoveries higher than the MQO limits were qualified with the failed matrix spike and high bias flags (FMS and HIB). Analytical results were considered invalid (INV) and qualified when the analyte was undetected and recoveries for associated matrix spike samples were less than 10%. Some PCB data were found to be invalid for this reason, but the *trans*-nonachlor surrogate recoveries were never below 10%.

To characterize contamination associated with field and analytical activities, field blanks were obtained for precipitation, particulate, and vapor samples at a subset of monitoring stations, and for dry deposition strips. For precipitation, particulate, and vapor samples, filters and/or absorbent were installed in the samplers for the normal sampling period but were not exposed to precipitation or air flow. The precipitation field blank included a water rinse of the collector surfaces to check for contamination by dry-deposited material that might have penetrated the cover and seal on the precipitation collector. Field blanks were not collected at all stations and potential station-specific contamination associated with these sites cannot be evaluated. However, contamination associated with sample collection, sampling equipment, sample processing, shipping, storing, and analysis can be evaluated based on the field blanks collected throughout the study.

PCB congeners were detected in all field blanks in all sample phases. This is not unexpected given the ubiquitous nature of PCBs in the environment. For *trans*-nonachlor determinations, 80% of the field blank results contained detectable concentrations of *trans*-nonachlor. When field blank concentrations were within a factor of five of the concentration in an associated sample, the sample result was qualified with the failed field blank flag (FFR) and also with the high bias flag (HIB). When sample concentrations were indistinguishable from the associated field blank concentration, samples were determined to be invalid and were qualified as such (INV). For PCBs in dry deposition, 30% of sample results were qualified as invalid, based on field blank contamination. For *trans*-nonachlor, 23% of the sample results for all phases were qualified as invalid, based on field blank contamination. Due to contaminated field blanks and variable sample results for field duplicates, many of the PCB results for samples collected from the bow of the *R/V Lake Guardian* in 1994 were determined to be invalid and are qualified as such, based on the potential for a shipboard source of PCB contamination (Miller, 1999). Samples collected from the yardarm of the *R/V Lake Guardian* and samples collected in 1995 were not affected.

For dry deposition samples, field blanks were collected with each sample and exposed to ambient conditions only for the length of time (<30 minutes) required to set up the routine dry deposition samples. Once the strips for the routine samples were set up, the field blank strips were returned to their sealed containers for the duration of the routine sampling episode. Because each sample had an associated field blank, the surface-area-normalized deposition of PCBs was subtracted from the corresponding field sample to minimize artifacts associated with sorption of gas-phase organic chemicals to the grease coating the deposition strips. When normalized to exposed surface area, the field blanks for land sites (n=35)

averaged 5100 ng/m^2 for total PCBs and the blanks for over-water sites (n=11) averaged 4700 ng/m^2 (Franze *et al*., 1998).

Laboratory blanks were prepared and analyzed for PCBs and *trans*-nonachlor in all phases. PCB congeners were detected in all laboratory blanks in all sample phases. For example, all results reported for PCB 1 for samples analyzed at Illinois Water Survey were determined to be invalid by the PI, based on erratic laboratory background. Thus, the PCB 1 results were not included in the repotted total PCB concentrations. When laboratory blank contamination was greater than the method detection limit, all of the associated results were qualified with failed blank sample (FBS) and high bias (HIB). No laboratory blanks contained *trans*-nonachlor above the method detection limit.

As discussed in Section 2.7, data verification was performed by comparing all field and QC sample results produced by each PI with the MQOs and with overall LMMB Study objectives. Analytical results were qualified when pertinent QC sample results did not meet the acceptance criteria defined by the MQOs. These flags were not intended to suggest that data were not useable; rather they were intended to caution the user about an aspect of the data that did not meet the predefined criteria. Tables 3-22 to 3-24 summarize the flags applied to the atmospheric PCB and *trans*-nonachlor data generated by each of the PIs involved in the analysis of atmospheric samples. Table 3-23 addresses data generated at the Illinois Water Survey. Table 3-23 addresses data generated at Indiana University. Table 3-24 addresses data generated for dry deposition samples. Qualifier flags were not applied to the data for total PCBs because they were the results of calculations rather than laboratory analyses.

The summary tables include the flags that directly relate to evaluation of the MQOs to illustrate some aspects of data quality, but do not include all flags applied to the data to document sampling and analytical information, as discussed in Section 2.7. As noted throughout this report, given the large number of PCB congeners that were determined by the investigators in this study, it is not practical to summarize the results for every congener.

As illustrated in Tables 3-23 and 3-24 and discussed in previous sections, PCB congeners and *trans*-nonachlor were not detected in a substantial portion of precipitation samples. Particulate and vapor samples more frequently contained PCB congeners and *trans*-nonachlor above detection limits than precipitation samples. Fifty-one percent of precipitation samples analyzed at Illinois Water Survey (Table 3-22) contained PCB 33 below detection limits and were qualified with the MDL flag (less than method detection limit) and 25% were qualified with the UND flag (analyte not detected). Sixty-four percent of precipitation samples analyzed at Indiana University (Table 3-23) contained PCB 180 below detection limits and were qualified with the MDL flag and PCB 180 was not detected in 21% of precipitation samples.

Of the three PCB congeners, PCB 33 was most frequently below detection limits for precipitation samples analyzed at Illinois Water Survey, whereas PCB 180 was most frequently below detection limits for precipitation samples analyzed at Indiana University.

Table 3-22. Field Sample Flags Applied to Select PCB Congeners and *trans*-Nonachlor Results in Atmospheric Samples Analyzed at Illinois Water Survey

Analyte	Fraction	Flags										
		Sensitivity		Contamination		Holding Time	Precision	Bias				Invalid
		MDL	UND	FFR	FBS	EHT	FFD	FPC	FSS	FMS	HIB	INV
PCB 33	Particulate	5% (11)	0.5% (1)	0.5% (1)	0	0.5% (1)	0	2% (5)	0.5% (1)	4% (8)	0	5% (11)
	Precipitation	51% (91)	25% (44)	0	0	46% (82)	1% (2)	0	1% (2)	5% (9)	0	0
	Vapor	0.8% (2)	0.8% (2)	0	3% (8)	5% (13)	0.4% (1)	6% (16)	0.8% (2)	0	0	8% (19)
PCB 118	Particulate	2% (5)	0	1% (3)	0	0.5% (1)	0	2% (5)	0.5% (1)	0	0	5% (11)
	Precipitation	11% (20)	0.6% (4)	0	5% (8)	46% (81)	0.6% (1)	0	0.6% (1)	0	0	0
	Vapor	0	0	0	16% (42)	5% (13)	1% (4)	6% (16)	1% (3)	0	0	7% (19)
PCB 180	Particulate	8% (18)	0.9% (2)	0.5% (1)	11% (23)	0.5% (1)	0	2% (5)	0.5% (1)	0	0	5% (11)
	Precipitation	28% (50)	5% (8)	0	10% (18)	46% (82)	0.6% (1)	0	0.6% (1)	0	0	0
	Vapor	1% (4)	1% (3)	0.4% (1)	34% (91)	5% (13)	1% (3)	6% (16)	1% (3)	0	0.4% (1)	7% (19)
trans-nonachlor	Particulate	35% (75)	16% (34)	0	0	0.5% (1)	0	0	0	0	0	0
	Precipitation	78% (151)	55% (106)	0	0	0.5% (1)	0	0	0	14% (27)	0	0
	Vapor	8% (21)	7% (19)	0.7% (2)	0	0.7% (2)	0.7% (2)	0	0	3% (8)	0	0

The number of routine field samples flagged is provided in parentheses. The summary provides only a subset of applied flags and does not represent the full suite of flags applied to the data.

MDL = Less than method detection limit (Analyte produced an instrument response but reported value is below the calculated method detection limit. Validity of reported value may be compromised.)
UND = Analyte not detected (Analyte produced no instrument response above noise.)
FFR = Failed field blank (A field blank sample, type unknown, associated with this analysis failed the acceptance criteria. It is unknown whether the blank that failed was a field blank or a lab blank. Validity of reported value may be compromised.)
FBS = Failed blank sample (A blank sample associated with this analysis failed the acceptance criteria. It is unknown whether the blank that failed was a field blank or a lab blank. Validity of reported value may be compromised.)
EHT = Exceeded holding time (Sample or extract was held longer than the approved amount of time before analysis. Validity of reported value may be compromised.)
FFD = Failed field duplicate (A field duplicate associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)
FPC = Failed performance check (A laboratory performance check sample associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)
FSS = Failed surrogate (Surrogate recoveries associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)
FMS = Failed matrix spike (A matrix spike associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)
HIB = Likely biased high (Reported value is probably biased high as evidenced by LMS (lab matrix spike) results, SRM (standard reference material) recovery, blank contamination, or other internal lab QC data. Reported value is not considered invalid.)
INV = Reported value is deemed invalid by the QC Coordinator.

Table 3-23. Field Sample Flags Applied to Select PCB Congener and *trans*-Nonachlor Results in Atmospheric Samples Analyzed at Indiana University

Analyte	Fraction	Flags										
		Sensitivity		Contamination		Holding Time	Precision	Bias				Invalid
		MDL	UND	FFR	FBS	EHT	FFD	FPC	FSS	FMS	LOB	HIB
PCB 33	Particulate	7% (1)	0	21% (3)	0	0	0	NA	0	0	0	0
	Precipitation	7% (1)	0	7% (1)	14% (2)	0	7% (1)	NA	0	0	7% (1)	0
	Vapor	0	0	19% (5)	62% (16)	0	0	NA	0	0	4% (1)	19% (5)
PCB 118	Particulate	43% (6)	0	14% (2)	1	0	0	NA	0	0	0	0
	Precipitation	57% (8)	0	7% (1)	1	0	0	NA	0	0	7% (1)	0
	Vapor	4% (1)	0	23% (6)	6	0	12% (3)	NA	0	0	4% (1)	12% (3)
PCB 180	Particulate	21% (3)	36% (5)	0	7% (1)	0	0	NA	0	0	0	0
	Precipitation	64% (9)	21% (3)	7% (1)	7% (1)	0	7% (1)	NA	0	0	7% (1)	0
	Vapor	4% (1)	31% (8)	12% (3)	8% (2)	0	23% (6)	NA	0	8% (2)	4% (1)	0
trans-nonachlor	Particulate	25% (1)	50% (2)	0	0	0	0	NA	25% (1)	0	0	0
	Precipitation	79% (11)	21% (3)	7% (1)	0	0	0	NA	0	29% (4)	7% (1)	0
	Vapor	26% (9)	0	0	0	3% (1)	0	NA	15% (5)	5	3% (1)	6% (2)

The number of routine field samples flagged is provided in parentheses. The summary provides only a subset of applied flags and does not represent the full suite of flags applied to the data.

MDL = Less than method detection limit (Analyte produced an instrument response but reported value is below the calculated method detection limit. Validity of reported value may be compromised.)
UND = Analyte not detected (Analyte produced no instrument response above noise.)
FFR = Failed field blank (A field blank sample, type unknown, associated with this analysis failed the acceptance criteria. It is unknown whether the blank that failed was a field blank or a lab blank. Validity of reported value may be compromised.)
FBS = Failed blank sample (A blank sample associated with this analysis failed the acceptance criteria. It is unknown whether the blank that failed was a field blank or a lab blank. Validity of reported value may be compromised.)
EHT = Exceeded holding time (Sample or extract was held longer than the approved amount of time before analysis. Validity of reported value may be compromised.)
FFD = Failed field duplicate (A field duplicate associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)
FPC = Failed performance check (A laboratory performance check sample associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)
FSS = Failed surrogate (Surrogate recoveries associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)
FMS = Failed matrix spike (A matrix spike associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)
LOB = Likely biased low (Reported value is probably biased low as evidenced by LMS (lab matrix spike) results, SRM (standard reference material) recovery or other internal lab QC data. Reported value is not considered invalid.)
HIB = Likely biased high (Reported value is probably biased high as evidenced by LMS (lab matrix spike) results, SRM (standard reference material) recovery, blank contamination, or other internal lab QC data. Reported value is not considered invalid.)
NA = This flag was not applied to this data set or this type of QC sample was not prepared and analyzed.

Table 3-24. Field Sample Flags Applied to Select PCB Congener and *trans*-Nonachlor Results in Dry Deposition Atmospheric Samples

Analyte	Flags									
	Sensitivity		Contamination		Holding Time	Precision	Bias			Invalid
	MDL	UND	FFB	EHT	FFD	FMS	FSS	HIB	FPC	INV
PCB118	37% (15)	0	68% (28)	2% (1)	0	49% (20)	0	27% (11)	0	68% (28)
PCB180	0	0	90% (38)	2% (1)	0	48% (20)	0	48% (20)	0	90% (38)
trans-nonachlor	70% (28)	8% (3)	48% (19)	3% (1)	0	10% (4)	0	0	0	48% (19)

The number of routine field samples flagged is provided in parentheses. The summary provides only a subset of applied flags and does not represent the full suite of flags applied to the data.

MDL = Less than method detection limit (Analyte produced an instrument response but reported value is below the calculated method detection limit. Validity of reported value may be compromised.)
UND = Analyte not detected (Analyte produced no instrument response above noise.)
FFB = A field matrix blank associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.
EHT = Exceeded holding time (Sample or extract was held longer than the approved amount of time before analysis. Validity of reported value may be compromised.)
FFD = Failed field duplicate (A field duplicate associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)
FMS = Failed matrix spike (A matrix spike associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)
FSS = Failed surrogate (Surrogate recoveries associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)
HIB = Likely biased high (Reported value is probably biased high as evidenced by LMS (lab matrix spike) results, SRM (standard reference material) recovery, blank contamination, or other internal lab QC data. Reported value is not considered invalid.)
FPC = Failed performance check (A laboratory performance check sample associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)
INV = Reported value is deemed invalid by the QC Coordinator.

Note: PCB 33 was not determined in the dry deposition samples.

For dry deposition samples, 37% contained PCB 118 below detection limits and were qualified with the MDL flag. However, PCB 118 was detected in all of the samples (i.e., none of the sample results were qualified with the undetected flag). For *trans*-nonachlor, 78% of the precipitation samples analyzed at Illinois Water Survey contained *trans*-nonachlor below detection limits and were qualified the MDL flag and in 55% of precipitation samples *trans*-nonachlor was not detected. Seventy-nine percent of precipitation samples analyzed at Indiana University contained *trans*-nonachlor below detection limits and were qualified the MDL flag and in 21% of samples *trans*-nonachlor was not detected. Seventy percent of dry deposition samples contained *trans*-nonachlor below detection limits and in 8% of dry deposition samples, *trans*-nonachlor was not detected.

A substantial portion of precipitation samples were flagged for exceeding sample holding times for determination of PCB congeners. For example, 46% of precipitation samples analyzed for PCB congeners at Illinois Water Survey exceeded the established holding time. However, the holding times for PCBs and many other environmental pollutants are not well-established and the effects on the sample results generally are not known. PCBs are highly stable compounds and loss or degradation is considered minimal even after 12 months if the samples are stored frozen. Loss or degradation rates may vary among congeners, depending on the mechanism (e.g., biological transformation, evaporative loss, or photolysis).

To characterize contamination associated with field and analytical activities, field blanks were obtained for precipitation, particulate, and vapor samples at a subset of monitoring stations, and for dry deposition strips.

For the analyzed at Illinois Water Survey, 1% or less of sample results for PCBs and *trans*-nonachlor were associated with field blanks that showed significant contamination and were qualified with the failed field blank flag. A single result for PCB 180 in a vapor sample also was qualified with the high bias flag due to this contamination. For the vapor samples analyzed at Indiana University, 23 % or less of sample results were associated with field blanks that showed significant contamination and were qualified with the failed field blank and high bias flags. Laboratory blanks also showed contamination for PCB congeners in all phases. Vapor samples were most frequently flagged for laboratory blank contamination with 62% of vapor sample results for PCB 33 generated at Indiana University being qualified with the failed laboratory blank flag and 34% of sample results for PCB 180 generated at Illinois Water Survey being qualified with the failed laboratory blank flag. As a result of contamination, 19% of the vapor sample results for PCB 33 also were qualified the high bias flag.

Contamination was a significant issue for PCB congeners and *trans*-nonachlor in dry deposition samples. The majority of dry deposition sample results are flagged for contamination and invalidated. Invalid sample results will not be used in the LMMB model. Due to the ubiquitous nature of PCBs, contamination can be an issue when analyzing samples with concentrations close to the method detection limit. Overall, the large majority of sample results were not affected by contamination.

Field duplicates were collected and analyzed for all phases. Although field duplicates were not planned for dry deposition, one field duplicate was collected. However, the dry deposition field duplicate was not used to evaluate study data. For the samples analyzed at Illinois Water Survey, less than 1% of all the field samples had associated duplicates with results outside the MQO limit and thus were qualified with the failed field duplicate flag. For the samples analyzed at Indiana University, 23% of vapor samples analyzed for PCB 180 had associated field duplicates with results outside the MQO limit and were qualified with the failed field duplicate flag. Only one precipitation sample for PCB 180 and one for PCB 33 had an associated field duplicate outside the MQO limit.

Matrix spike samples results showed acceptable results for the large majority of study samples in all phases, except for dry deposition. For samples analyzed at Illinois Water Survey, all of the spike

recoveries for all sample results for PCB 118 and PCB 180 in all phases were within MQO limits. For *trans*-nonachlor, 14% of the precipitation sample results were qualified with the failed matrix spike flag for samples analyzed at Illinois Water Survey. For samples analyzed at Indiana University, all of the spike recoveries for all sample results for PCB 33 and PCB 118 in all phases were within MQO limits. For *trans*-nonachlor, 29% of precipitation sample results were qualified with the failed matrix spike flag for samples analyzed at Indiana University. For analysis of PCBs and *trans*-nonachlor in dry deposition samples, matrix effects presented analytical difficulties and 48% of the sample results were qualified with the failed matrix spike flag for PCB 180 and 10% for *trans*-nonachlor.

Surrogate recoveries indicated acceptable results for the large majority of study samples. Of the results for PCBs 33, 118, and 180 generated at the Illinois Water Survey, at most 1% of the vapor, precipitation, and particulate samples were qualified with the failed surrogate spike flag (FSS). None of the *trans*-nonachlor results generated at the Illinois Water Survey failed the surrogate recovery limits. None of the results for PCBs 33, 118, or 180 analyzed at Indiana University failed the surrogate recovery limits, but 15% of the vapor samples and 25% of the particulate-phase samples analyzed there for *trans*-nonachlor failed the surrogate recovery limits. As noted earlier in this section, the surrogate recoveries for the dry deposition results were erratic and subject to interferences. As a result, no results for dry deposition samples were qualified due to surrogate recovery problems and no surrogate recovery correction was applied to the dry deposition results for any analyte.

As discussed in Section 1.5.5, MQOs were defined in terms of six attributes: sensitivity, precision, accuracy, representativeness, completeness, and comparability. GLNPO derived its data quality assessments based on a subset of these attributes. For example, system precision was estimated as the mean relative percent difference (RPD) between the results for field duplicate pairs. Similarly, analytical precision was estimated as the mean relative percent difference (RPD) between the results for laboratory duplicate pairs. Tables 3-25 to 3-28 provide summaries of data quality assessments for several of these attributes for the data for atmospheric PCB congener 33, 118, and 180 and *trans*-nonachlor.

Data quality assessments were conducted for two separate sets of results: those sample results that are above 5 times the sample specific detection limits and those sample results that are below 5 times the sample specific detection limits. Performing separate assessment illustrates the expected differences in data quality for these sample groups that are due to increased variability in the analytical results when sample concentrations are close to the detection limit of the analytical method. In addition, MQOs often were set and applied differently for sample results that are greater than 5 times the detection limit versus those results that are less than five times the method detection limit.

As discussed in this chapter, a significant number of sample results were below the calculated analytical sample specific method detection limits. Seven percent of precipitation samples analyzed at Indiana University were reported below the MDL and 51% of precipitation samples analyzed at Illinois Water Survey were reported as below the MDL. For PCB 180, 86% of precipitation samples analyzed at Indiana University were below the sample specific detection limits. For study samples that are below detection limits, the variability of sample results is expected to be greater than for sample results that are significantly above the detection limit and in the middle of the calibration range of the analytical method. Data quality assessments based on field duplicates and laboratory duplicates also will reflect increased variability because the sample concentrations are close to or below the detection limits.

System precision, estimated as the mean RPD between field duplicate results, varied by fraction. For example, for PCB 118 particulate-phase samples analyzed at Illinois Water Survey, with results greater than 5 times their associated sample specific MDL, had a mean RPD of 21% and vapor samples analyzed at Illinois Water Survey, with results greater than 5 times their associated sample specific MDL, had a mean RPD of 54%. System precision also varied by the relationship of sample concentrations to the

sample specific detection limits. For example, for vapor-phase samples analyzed at Indiana University for PCB 180, the mean RPD was 42% for sample results less than 5 times the sample specific detection limit and was 22% for sample results greater than 5 times the sample specific detection limit. Similarly, for vapor-phase samples analyzed at Indiana University for *trans*-nonachlor, the mean RPD was 53% for sample results less than 5 times the sample specific detection limit and was 16% for sample results greater than 5 times the sample specific detection limit.

In some cases, the system precision was unexpectedly greater for sample results at higher concentrations. For example, for vapor samples analyzed at Illinois Water Survey, the mean RPD was 21% for sample results less than 5 times the sample specific detection limit and was 40% for sample results greater than 5 times the sample specific detection limit. System precision also varied by congener, although a pattern among congeners was not evident. For example, for precipitation samples analyzed at Indiana University, the mean RPD was 34% for PCB 118 and was 53% for PCB 180, whereas for particulate samples, the mean RPD was 55% for PCB 118 and was 23% for PCB 180. Duplicate pair samples with a reported concentration of zero for either one of both samples could not be used in this assessment. Because of the large number of results reported as zero, the system precision estimate is based on only a small number of field duplicates and may not accurately reflect the system.

Analytical precision, estimated as the mean RPD between laboratory duplicates, only could be estimated for a single particulate sample analyzed at Indiana University (a small number of laboratory duplicates prepared and analyzed for these analytes in the study because of the large expense of these analyses). The RPD between laboratory duplicates of particulate sample was 13% for PCB 33 and 34% for PCB 118. This analytical precision for particulate samples was lower than the mean RPD for system precision, where the mean RPD was 31% for PCB 33 and 55% for PCB 118.

Evaluation of matrix spike sample (LMS) recoveries shows a slight low bias overall for all PCB congeners for phases of atmospheric samples, except dry deposition. For vapor samples, the mean LMS recovery for PCB 33 was 93% for samples analyzed at Indiana University and at the Illinois Water Survey. For PCB 180 in vapor samples, the mean LMS recovery was 94% for samples analyzed at Illinois Water Survey and 96% for samples analyzed at Indiana University. For precipitation samples, the mean LMS recovery for PCB 33 was 86% for samples analyzed at Illinois Water Survey and 91% for samples analyzed at Indiana University. For *trans*-nonachlor, the low bias was more pronounced. For example, for vapor samples, the mean LMS recovery was 80% for samples analyzed at Illinois Water Survey and 70% for samples analyzed at Indiana University.

For dry deposition, a significant high bias was observed based on results of the LMS samples. For PCBs 118 and 180, the mean LMS recoveries were 626% and 10,798 % . For *trans*-nonachlor, the bias was much less extreme, with a mean LMS recovery of 126%. Sample results associated with LMS results that were outside the MQO were qualified with the failed matrix spike and high bias flags. As discussed above, a significant portion of sample results for dry deposition were determined to be invalid based on results of LMS and other QC samples. For the majority of PCB and *trans*-nonachlor results, the PI and QC coordinator determined that the bias demonstrated by results for the LMS and other QC samples was not strong enough to warrant flagging the data as either HIB or LOB. As discussed above, the sample results that are flagged HIB are due, in part, to contamination in field and laboratory blanks.

Table 3-25. Data Quality Assessment for PCB 33 in Atmospheric Samples

Fraction (Lab)	Number of Routine Samples Analyzed	System Precision Mean Field Duplicate RPD (%)		Analytical		
				Precision	Bias	Sensitivity
		< 5 * MDL	> 5 * MDL	Mean Lab Duplicate RPD < 5* MDL	Mean LMS Recovery (%)	Samples reported as < MDL (%)
Vapor (Illinois)	251	(0)	34% (14)	(0)	93% (33)	0.80%
Precipitation (Illinois)	179	72% (3)	(0)	(0)	86% (23)	51%
Particulate (Illinois)	208	31% (10)	(0)	(0)	82% (28)	4.8%
Vapor (Indiana)	26	(0)	16% (13)	(0)	93% (14)	(0)
Precipitation (Indiana)	14	23% (11)	(0)	(0)	91% (14)	7.1%
Particulate (Indiana)	14	31% (8)	(0)	13% (1)	90% (13)	7.1%

The number of QC samples used in the assessment is provided in parentheses.
RPD= Relative percent difference
LMS= Laboratory matrix spike

Table 3-26. Data Quality Assessment for PCB 118 in Atmospheric Samples

Fraction (Lab)	Number of Routine Samples Analyzed	System Precision Mean Field Duplicate RPD (%)		Analytical		
				Precision	Bias	Sensitivity
		< 5 * MDL	> 5 * MDL	Mean Lab Duplicate RPD < 5* MDL	Mean LMS Recovery (%)	Samples reported as < MDL (%)
Vapor (Illinois)	251	(0)	54% (14)	(0)	97% (34)	0
Precipitation (Illinois)	179	43% (8)	(0)	(0)	94% (23)	11%
Particulate (Illinois)	208	28% (8)	21% (2)	(0)	94% (28)	2.4%
Vapor (Indiana)	26	45% (7)	34% (6)	(0)	96% (14)	3.9%
Precipitation (Indiana)	14	34% (11)	(0)	(0)	93% (14)	57%
Particulate (Indiana)	14	55% (8)	(0)	34% (1)	95% (13)	43%
Dry deposition	13	(0)	(0)	(0)	626% (5)	69%

The number of QC samples used in the assessment is provided in parentheses.
RPD= Relative percent difference
LMS= Laboratory matrix spike

Table 3-27. Data Quality Assessment for PCB 180 in Atmospheric Samples

Fraction (Lab)	Number of Routine Samples Analyzed	System Precision Mean Field Duplicate RPD (%)		Analytical		
				Precision	Bias	Sensitivity
		< 5 * MDL	> 5 * MDL	Mean Lab Duplicate RPD < 5* MDL	Mean LMS Recovery (%)	Samples reported as < MDL (%)
Vapor (Illinois)	251	21%(3)	40% (11)	(0)	94% (34)	1.6%
Precipitation (Illinois)	179	47% (9)	(0)	(0)	93% (23)	29%
Particulate (Illinois)	208	33% (9)	10% (1)	(0)	97% (28)	8.2%
Vapor (Indiana)	26	42% (3)	22% (2)	(0)	96% (14)	35%
Precipitation (Indiana)	14	53% (7)	(0)	(0)	92% (14)	86%
Particulate (Indiana)	14	23%(5)	(0)	(0)	95% (13)	57%
Dry deposition	13	(0)	(0)	(0)	10,798% (5)	0

The number of QC samples used in the assessment is provided in parentheses.
RPD= Relative percent difference
LMS= Laboratory matrix spike

Table 3-28. Data Quality Assessment for *trans*-Nonachlor in Atmospheric Samples

Fraction (Lab)	Number of Routine Samples Analyzed	System Precision Mean Field Duplicate RPD (%)		Analytical		
				Precision	Bias	Sensitivity
		< 5 * MDL	> 5 * MDL	Mean Lab Duplicate RPD < 5* MDL	Mean LMS Recovery (%)	Samples reported as < MDL (%)
Vapor (Illinois)	270	all results =0	24% (23)	(0)	80% (36)	7.8%
Precipitation (Illinois)	193	all results = 0	(0)	(0)	73% (23)	78%
Particulate (Illinois)	217	52% (10)	(0)	(0)	75% (28)	34%
Vapor (Indiana)	34	53% (10)	16% (2)	(0)	70% (18)	27%
Precipitation (Indiana)	14	66% (8)	(0)	(0)	75% (14)	100%
Particulate (Indiana)	4	all results = 0	(0)	54% (1)	70% (13)	75%
Dry deposition	21	(0)	(0)	(0)	126% (5)	81%

The number of QC samples used in the assessment is provided in parentheses.
RPD= Relative percent difference
LMS= Laboratory matrix spike

3.3 Data Interpretation

3.3.1 Atmospheric Sources

Atmospheric sources of PCBs and *trans*-nonachlor to Lake Michigan can include exchange of contaminants from the vapor phase to the water, deposition of contaminants associated (e.g., bound or sorbed) with particulates, and contaminants in precipitation. This report summarizes the concentrations of PCB congeners, total PCBs, and *trans*-nonachlor reported during the LMMB Study in each of these atmospheric phases: vapor, particulate, dry deposition, and precipitation. The data for these phases will be used in the LMMB modeling efforts to evaluate the fluxes and loads of contaminants from each of these sources.

PCBs and *trans*-nonachlor were detected in samples from all four atmospheric phases. PCBs were detected above the sample-specific detection limits most frequently in the vapor-phase samples, followed by the particulate-phase samples, and least often in the precipitation samples. This is consistent with the findings of researchers that have estimated the atmospheric fluxes of PCB from the vapor and particulate phase as much higher than from wet deposition (Franz *et al.*, 1998).

While PCBs were detected in all four atmospheric phases, the frequency of occurrence and magnitude of concentrations differed among the PCB congeners and among the four phases. Figure 3-19 shows the mean percentage of individual PCB congeners that contributed to the total PCB concentration in vapor, particulate, and precipitation phases. In the vapor phase, the lower molecular weight, less-chlorinated congeners predominated, while particulate and precipitation phases contained a more diverse mixture of PCB congeners, including higher molecular weight congeners. Baker and Eisenreich (1990) also found that the more volatile tri- and tetrachlorobiphenyl congeners dominated the distribution of PCBs in the atmospheric gas phase. The higher vapor pressures of these less-chlorinated PCB congeners favor volatilization from the particulate and dissolved phases to the vapor phase. The differences in vapor pressures among the PCB congeners may explain some of the differences in the frequencies of occurrence of PCB congeners in the various phases. For example, the more volatile PCB 33 was less often detected in the precipitation phase than the less volatile, more chlorinated PCB 180 (Figure 3-20).

To statistically evaluate the contribution of the various PCB congeners, the proportion of the total PCB concentration attributed to the higher chlorinated (high molecular weight) congeners was calculated for vapor-phase, particulate-phase, and precipitation samples. For the purposes of this evaluation, the higher chlorinated congeners include the hexachloro-, heptachlor-, octachloro, and nonachlorobiphenyl congeners, while the lower chlorinated congeners include the dichloro-, trichloro-, tetrachloro-, and pentachlorobiphenyl congeners. Neither the three monochlorobiphenyl congeners nor the one decachlorobiphenyl congener were reported by all laboratories in all phases, so they were not included in this calculation.

The high molecular weight proportion was calculated as:

$$\text{High molecular weight proportion} = \frac{\sum(Cl_6 + Cl_7 + Cl_8 + Cl_9)}{\sum(Cl_2 + Cl_3 + Cl_4 + Cl_5 + Cl_6 + Cl_7 + Cl_8 + Cl_9)}$$

Figure 3-19. Mean Percentage of Individual PCB Congener's Contribution to Total PCB Concentrations

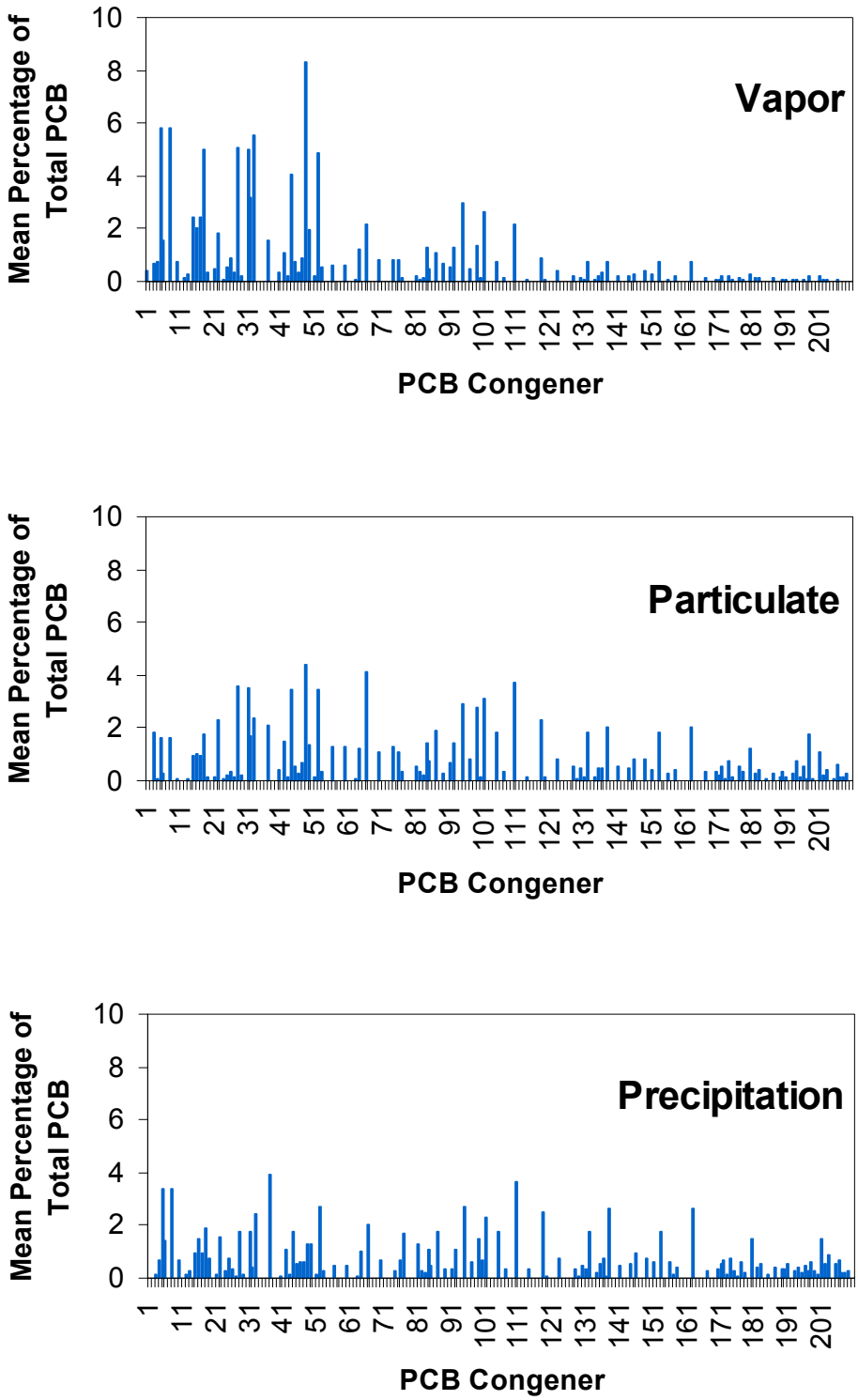
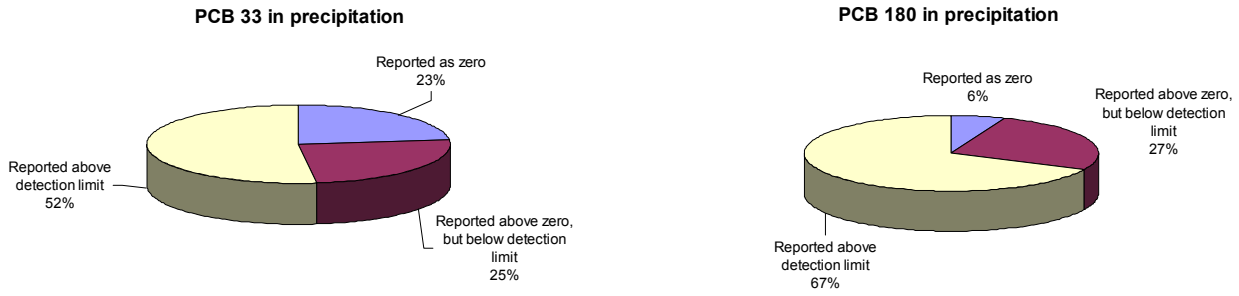


Figure 3-20. Percentages of PCBs 33 and 180 in Precipitation Samples Reported as Zero, Below the Detection Limits, and Above the Detection Limits



There were three instances in which two or more congeners in the two categories coeluted and could not be reported separately (PCBs 123 and 149; PCBs 111 and 131; and PCBs 105, 132, and 153), therefore, none of the results for these congeners were used to calculate the proportions.

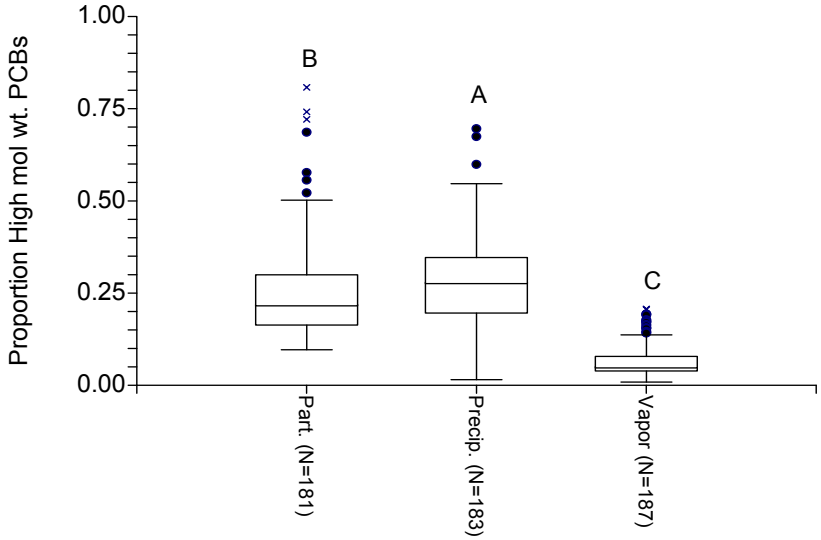
Based on a comparison of high molecular weight proportions in over 180 vapor, particulate, and precipitation samples, there was a significant difference among the three phases (Figure 3-21). Precipitation samples had the highest proportion of high molecular weight PCB congeners, followed by particulate-phase samples. Vapor-phase samples contained the lowest proportion of high molecular weight PCB congeners, consistent with the lower vapor pressures of the higher molecular weight congeners.

Similarly to the low molecular weight PCB congeners, *trans*-nonachlor, which has a high vapor pressure also was more prevalent in the vapor phase than in precipitation or the particulate phase. Mean vapor-phase concentrations of *trans*-nonachlor were approximately 10 to 20 times higher than the particulate-phase concentrations at the same sampling stations (see Tables 3-7 and 3-13). *trans*-Nonachlor was even less common in precipitation samples. With the exception of the IIT Chicago site, 75 to 100% of precipitation samples from the various LMMB sampling stations contained *trans*-nonachlor below the sample-specific detection limit.

3.3.2 Atmospheric Concentrations

In this study, total PCB concentrations in the vapor phase ranged from 0 to 6300 pg/m^3 at shoreline sampling stations surrounding Lake Michigan. Average monthly composite concentrations of total PCBs ranged from 320 to 2600 pg/m^3 at these stations. These concentrations are comparable to vapor-phase total PCB concentrations measured by other researchers over large water bodies near urban influences. Brunciak *et al.* (2001) measured average vapor-phase total PCB concentrations of 1180 pg/m^3 near Baltimore, MD and 550 pg/m^3 over the Northern Chesapeake Bay. Similarly, vapor-phase total PCB concentrations ranged from 210 to 4780 pg/m^3 over Galveston Bay, TX (Park *et al.*, 2001). The lower PCB concentrations measured at the more remote out-of-basin sampling stations in the LMMB Study (averaging 110 to 260 pg/m^3) were comparable to concentrations measured by other researchers at remote sites across the northern hemisphere. Iwata *et al.* (1993) measured average vapor-phase total PCB concentrations of 93, 130, 130, 320, and 290 pg/m^3 over the Bering Sea, Gulf of Alaska, North Pacific Ocean, Caribbean Sea, and North Atlantic Ocean, respectively.

Figure 3-21. Proportion of High Molecular Weight PCB Congeners in the Vapor Phase, Particulate Phase, and Precipitation



Boxes represent the 25th percentile (bottom of box), 50th percentile (center line), and 75th percentile (top of box) results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. The ^s represent results beyond 3*IQR from the box. The letters (A - D) above the boxes represent the results of the analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05). Proportions were transformed by calculating the arcsine of the square root of the proportion prior to testing.

The range of vapor-phase total PCB concentrations measured in the LMMB Study during 1994 and 1995 also are relatively consistent with PCB concentrations historically measured in the Great Lakes region. Baker and Eisenreich (1990) reported average atmospheric PCB concentrations over the Great Lakes of 300 to 3200 pg/m^3 with no discernable trend from 1977 through 1986. Baker and Eisenreich (1990) concluded that PCB concentrations have remained relatively constant in the atmosphere over this period. In 1986, Baker and Eisenreich (1990) measured an average PCB concentration of 1200 pg/m^3 over Lake Superior. Hoff *et al.* (1992) measured monthly averages of 55 to 823 pg/m^3 over Southern Ontario in 1988 to 1989. Also in 1989, Hornbuckle *et al.* (1993) measured average total PCB concentrations of 670 to 2200 pg/m^3 over southern Green Bay, and 160 to 520 pg/m^3 over northern Green Bay in 1989. From 1991 to 1993, Hornbuckle *et al.* (1995) measured 30 to 400 pg/m^3 of total PCB in air samples collected at the Sleeping Bear Dunes site. PCB concentrations measured in the LMMB Study during 1994 and 1995 are consistent with the range of previous measurements and do not clearly suggest trends of increasing or decreasing PCB concentrations in the vapor phase, however, as Hoff *et al.* (1992) noted, such long-term trends may be difficult to detect due to the large amplitude of seasonal cycles and due to differences in sampling locations and analytical methodologies in the various studies. Using longer-term monitoring data and consistent IADN (Integrated Atmospheric Deposition Network) monitoring stations, Simcik *et al.* (1999) were able to detect decreases in vapor-phase total PCB concentrations from 1991 to 1997 over Lake Michigan and Lake Erie, with half-lives of 2.8 to 3.3 years.

Total PCB concentrations in precipitation averaged 1.3 to 16 ng/L at shoreline sampling stations and 0.29 to 1.7 ng/L at out-of-basin stations during the LMMB Study. These values also were relatively consistent with total PCB concentrations measured in precipitation over other large water bodies across the U.S. Leister and Baker (1994) measured a volume-weighted mean total PCB concentration of 1.6 ng/L in

precipitation over the Chesapeake Bay, and Park *et al.* (2001) measured total PCB concentrations of 0.08 to 3.34 ng/L in precipitation over Galveston Bay, TX. Total PCB concentrations in snowfall at Lake Tahoe ranged from 4.8 to 5.1 ng/L (Datta *et al.*, 1998). In the Great Lakes region, Simcik *et al.* (2000) reported lower PCB concentrations in precipitation over Lake Michigan and Lake Erie than over Lake Huron and Lake Ontario. Simcik *et al.* (2000) also reported significant decreases in PCB concentrations in precipitation over Lake Michigan from 1991 to 1997, with a half life of 6.9 years.

3.3.3 Seasonality

Concentrations of PCBs in the vapor phase were highly influenced by season (Figure 3-2). Total PCB concentrations and individual congeners (PCB 118 and PCB 180) in the vapor phase peaked in mid summer and reached minimum values in the winter. The mean total PCB concentration during the summer at shoreline and out-of-basin stations was eight times higher than in the winter. *trans*-Nonachlor followed the same trend, with vapor-phase mean concentrations in summer ten times higher than in the winter. This finding is consistent with other researchers who have measured PCBs and chlordanes over annual cycles (Hoff *et al.*, 1992; Green *et al.*, 2000). Hoff *et al.* (1992) concluded that this seasonal pattern was due to volatilization and the effects of temperature and vapor pressures on the distribution of these organic contaminants in the vapor phase. As temperature increases, distribution of these organic contaminants within the atmosphere favors the vapor phase. Fluxes of PCBs from Lake Michigan to the atmospheric vapor phase also may increase vapor-phase PCB concentrations during the summer (Hornbuckle *et al.*, 1993).

In contrast, the particulate-phase total PCB concentrations exhibited a different seasonal pattern than the vapor-phase results (Figure 3-8). Particulate-phase total PCB concentrations were higher in spring and winter than in summer and autumn. The particulate-phase *trans*-nonachlor concentrations exhibited a different pattern than the corresponding vapor-phase results (Figure 3-9), and slightly different from the pattern for the particulate-phase total PCBs, with the highest concentrations in the winter. These patterns for total PCBs and *trans*-nonachlor also are consistent with the effects of temperature and vapor pressures, in that at the lower temperatures during winter, the contaminants are less likely to volatilize off of the surface of particulates into the vapor phase.

3.3.4 Regional Considerations

Atmospheric sampling stations in the LMMB Study were grouped into the following categories based on their proximity to urban areas: urban, urban-influenced, rural, and remote (see Table 2-6 in Chapter 2). Mean total PCB concentrations at urban sites were six times higher than at urban-influenced sites, seven times higher than at rural sites, and four times higher than at remote sites. The highest total PCB concentrations were at the IIT Chicago site (mean of 2600 pg/m^3), which is expected since various combustion sources and other sources are likely to be present in a large urban area. The second highest total PCB concentrations were at the remote Beaver Island location (mean of 970 pg/m^3), which was not anticipated and suggests an unknown source near this otherwise relatively remote site in northern Lake Michigan. The Beaver Island location had the highest concentrations of PCB 180 (mean of 11 pg/m^3), a highly chlorinated and relatively high molecular weight congener. Mean PCB 180 concentrations at Beaver Island were 3 times higher than at the IIT Chicago site and 33 to 46 times higher than at any other remote station. The high concentrations of relatively high molecular weight PCB congeners at the Beaver Island site suggest a nearby source, rather than long-range transport of PCBs from distant sources. However, a review of land use maps, literature sources, and other information was conducted during the preparation of this report. That review did not uncover any obvious sources. Therefore, rather than speculate about possible sources, the anomalous PCB results at Beaver Island are simply reported here.

Results were similar for particulate phase PCB concentrations, with the highest concentrations at the IIT Chicago and Beaver Island sites. Total PCB concentrations in precipitation also were highest at the IIT Chicago site, but precipitation-phase PCBs at Beaver Island were comparable to other remote sites.

The results from this study demonstrate that the urban source of PCBs from the Chicago area significantly influence PCB concentrations over Lake Michigan. A statistically significant difference in the vapor-phase concentrations of PCB 118 between over-water stations north and south of 43° latitude (Figure 3-6) was observed in this study. PCB concentrations over the southern portion of Lake Michigan, and particularly near Chicago, were significantly higher than concentrations over northern Lake Michigan. PCB 118 concentrations at over-water stations 1 and 6, near Chicago, were 6 to 39 times higher than at any other over-water station. PCB 118 concentrations at these two stations also were higher than at the IIT Chicago site.

Other researchers have noted a similar influence on atmospheric PCB concentrations over Lake Michigan due to the urban Chicago area. As a part of the AEOLOS (Atmospheric Exchange Over Lakes and Oceans) Project, Simcik *et al.* (1997) determined that gas-phase PCB concentrations over southern Lake Michigan were highly influenced by the urban/industrial area from Evanston, IL to Gary, IN. Emissions from these urban areas increased the average coastal atmospheric concentration above the continental background by a factor of four. Gas-phase PCB concentrations ranged from 0.14 ng/m^3 to 1.1 ng/m^3 over the lake and from 0.27 to 14 ng/m^3 in the urban area. Total PCB concentrations in rain measured by Offenberg and Baker (1997) over southern Lake Michigan ranged from 4.1 to 189 ng/L and were from 2 to 400 times higher than the measured regional background concentrations. Offenberg and Baker (1997) concluded that the "urban plume" of Chicago increases PCB wet deposition loadings over southern Lake Michigan by 50 to 400%.

In contrast to the PCB results, the vapor-phase *trans*-nonachlor concentrations suggest that there is a significant source in the rural, agricultural area near Bondville, with generally decreasing concentrations in more northern stations (Figure 3-5). *trans*-Nonachlor concentrations in the vapor phase were highest at the Bondville station followed by the IIT Chicago station. Although *trans*-nonachlor is no longer produced in the U.S., nor applied in agricultural practice, this apparent trend from south to north may indicate the effects of historical agricultural applications, with lesser contributions from other historical uses in urban areas such as Chicago.